

## **PHYSICO-CHEMICAL METHODS**

members of the staff of University College, Cork, we are indebted for valuable help and suggestions. In particular to Dr. M. D. McCarthy on mathematical problems, and to Dr. D. F. Kelly, Lecturer in Physical Chemistry, for general help during the preparation of the book.

The new chapter on High Pressure Technique has been written by Mr. R. Taylor, M.A.(Cantab.), B.Sc.(Oxon), Senior Scientific Officer, Chemical Research Laboratory, D.S.I.R. Low temperature problems have been reviewed by Mr. D. J. Williams. Where assistance has been obtained in smaller sections or in isolated points, acknowledgement has been made as far as possible in the text.

The authors desire to express their indebtedness to numerous journals, especially with regard to recent developments, and it is hoped that acknowledgement has always been recorded. They wish particularly to thank the Editor (H. E. Howe) of *Industry and Engineering Chemistry* for his personal interest and help. The *Journal of Scientific Instruments* and the *School Science Review*, to mention but two journals, have been found very useful. Numerous firms have freely co-operated and placed valuable information at our disposal. They are especially grateful to F. Twyman, F.R.S., and the research staff of Messrs. Hilger, Ltd., and to the Director of the National Physical Laboratory, London.

It is hoped that readers will continue, as in the past, to correspond with the authors, and any criticism of the book or suggestions for the next edition will be very welcome. Particularly in connection with the "Suggestions for Further Reading"—a new feature of the present edition—the authors will be grateful for offprints, suggestions and further references.

J. REILLY  
W. N. RAE

*December 1939*



## PREFACE TO THE SECOND EDITION

THE very favourable reception given to the first edition has encouraged the authors to develop the book still further on the general lines already indicated. With the entire re-setting of the type it has been possible to undertake a thorough revision of the text. Many modifications and additions have been made. By enlarging the size of the pages these improvements have been secured without undue increase in bulk. Twenty extra chapters and a large number of diagrams have been incorporated, with some rearrangement of subject-matter. The general aim has been to outline the technique used in the various applications of physical methods to chemical problems, and to indicate how difficulties have been overcome. The processes described can very often be applied in other directions than in those immediately indicated. The authors have endeavoured to make the book a standard work in the subject, and every effort has been made to secure accuracy in experimental details and in references. The writers make no claim to completeness on account of the wide scope of the subject, yet most branches of practical physical chemistry have been considered, especially those of technical importance.

Special acknowledgement is due to Professor Wilder D. Bancroft of Cornell University for many useful suggestions in his review of the first edition in the *Journal of Physical Chemistry*, to Professor T. M. Lowry, F.R.S., of Cambridge University, and to the Director of the National Physical Laboratory, London. The authors are also indebted to Mr. James Teegan for assistance, especially in the writing of the three chapters, 'The Thermionic Tube', 'The Raman Effect', and 'Dielectric Constants'. In the tedious work of proof-reading they had the aid of Mr. R. McCarthy, M.Sc., who also completed the chapter on Sublimation. Owing to the wide field covered, the authors have thought it advisable when possible to have the advice and help of specialists in various subjects, and acknowledgement is made in the text to such help. Numerous workers in Europe and in America have written expressing interest in the work and often indicating ways in which the usefulness of the book might be extended. In some cases it has been possible to modify the text on the lines indicated. A continuation of this helpful co-operation will be greatly appreciated.

J. REILLY  
W. N. RAE

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## PREFACE TO THE FIRST EDITION

SOME ten years ago, two of us, neither of whom had, at the time, a wide acquaintance with actual technical practice in Chemistry, met for the first time in a large works laboratory. We were struck by the numerous instances in which physico-chemical problems arise in such laboratories, and how in many cases it was difficult to find a good account of the more important methods employed in various branches of physical chemistry, and especially of work on precise physico-chemical measurements. On the one hand there were the books which were intended for student practice at the undergraduate stage, and these did not pretend to treat the subject from the point of view of the post-graduate or technical chemist. On the other hand there were the original papers of authors contained in the various scientific journals, but these in many cases were not readily accessible and the material was not correlated.

We agreed that a text-book which approached the subject of practical physical chemistry from the Industrial Chemists' standpoint was very desirable and would have been extremely useful to us, and we resolved that if at some time in the future the opportunity occurred we would attempt to provide or produce such a book. During the last ten years we have had considerable experience in technical and applied chemical work and with an additional colleague (T. S. W.) now offer the present work in the hope that it will be of real value to both technical chemists and post-graduate science students.

The choice of what would be treated and what omitted was to some extent influenced by the nature of the work on which the authors have been engaged. In different circumstances other points might be emphasized and certain branches considered in greater detail. The same remarks apply to the methods described: some may find that a favourite method is omitted and one which they dislike included. We trust, however, that the general consensus of opinion will favour our selection, as our aim has been to cover the main lines of activity in the subject.

The book, as indicated, is intended principally for the advanced student who desires to obtain a general knowledge of the subject, and for the investigator wishing to know the methods which have been applied to solve particular types of problems. Elementary detail has, therefore, been omitted in many sections, but some of the more important subjects have been treated extensively in order to illustrate more fully the general principles of precise measurement. While it is realized that minor details of manipulation generally cannot be learned from mere description, experience being here the great teacher, yet it is hoped that the descriptions of standard apparatus and special experiments outlined will be of use in the laboratory.

We have made free use of the standard text-books such as Ostwald, Arndt, Findlay, and Spencer, manufacturers' pamphlets, and also a large number of original papers. The abbreviations used in reference to journals, &c., have followed generally the lines adopted by the Chemical Society (London). In some instances special information, publications, and diagrams have been kindly supplied by authors and manufacturing and instrument-making firms. To these acknowledgements have been made in the text. Over 400 diagrams have been specially prepared for the book, and the authors are indebted to Mr. J. J. Sheehan, A.R.C.Sc.I., who has drawn about 100 of these figures.

The thanks of the authors are due to Mr. Brian J. McCarthy, A.R.C.Sc.I., for assistance with the chapter on Pumps (including related diagrams), to Mr. F. Fogarty, M.Sc., for assistance with the Distillation chapter, and to Mr. T. Crowley, B.Sc., for general help, especially in bringing up to date some of the chapters written or drafted during the war.

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J. REILLY

W. N. RAE

T. S. WHEELER

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# CHAPTER I

## THE LABORATORY

### SECTION 1: GENERAL PLAN

**THE BUILDING.** The planning of a building or unit for practical physical chemistry is influenced by the nature of the work to be undertaken, by the age and training of the workers, and by the resources available. The general teaching establishment will require a different arrangement from that of the industrial laboratory. The latter again will to some extent require a different design if it is planned for a works-control laboratory or as a general-research laboratory.

In the great majority of cases the physical-chemical worker will have his building provided with lay-out of laboratories ready planned. At most the arrangement of fittings and equipment will be his concern.<sup>1</sup> In the following brief discussion each section of the physical-chemical unit will be indicated.

### THE LABORATORIES

For completeness the following laboratories or sections are required, but of course the extent of the various sections, as already indicated, is governed largely by the financial aid available. In smaller establishments the general laboratory may serve to contain many of the auxiliary rooms or units suggested.

The usual requirements are :

- (a) Main laboratory
- (b) One or more smaller laboratories or rooms for special purposes  
such as :
  - Optical work
  - High-temperature experiments
  - Low-temperature experiments (liquid air)
  - Standardization work and storage of precision instruments
  - Conductivity work ; preparation of distilled water
  - X-ray work
  - Glass-blowers' work
- (c) Balance room
- (d) Electrical laboratory
- (e) Constant-temperature room
- (f) Dark room

<sup>1</sup> Munby, *Laboratories, their Planning and Fittings*, Bell, 1921.



- (g) Gas-analysis room
- (h) Workshop
- (i) Switchboard room and accumulator store
- (j) Preparation and wash-up room

In addition store rooms and storage for solvents, electric motors, pumps, transformers, &c., may be needed. In a self-contained unit a library, staff room, office, and other accommodation will also be necessary. In the case of educational establishments adequate lecture rooms with adjacent preparation rooms would also be required.

For special industries even further subdivision is often necessary. In the Brown-Firth Research Laboratories such subjects as 'corrosion', 'mechanical testing', 'refractories examination', 'gases and inclusions', 'pyrometric control', 'experimental melting', and 'carbides' have special laboratories. To indicate how extensive a research organization requires to be for thorough examination of even one branch, the following data are of interest. For the complete examination of an alloy the following information may be required.<sup>1</sup>

*Chemical analysis*

*Metallographic examination*

Macrostructure

Microstructure

Grain size

Examination of inclusions (quantitative and qualitative)

*Physical properties*

Melting and freezing temperatures

Critical points

Specific gravity

Specific heat

Thermal conductivity

Thermal expansion

Electrical conductivity

Thermoelectrical properties

Electrochemical potential

Magnetic properties

Optical properties

X-ray analysis

*Mechanical properties at normal temperatures*

Tensile (elastic limit, proof stress, yield point, maximum stress, elongation, reduction of area, elastic modulus, Poisson's ratio)

Hardness

Notched-bar impact

Torsion (elastic limit, yield point, maximum stress, degrees twist shear modulus)

Bend

Fatigue range

Deformation tests

Wear-resistance tests

<sup>1</sup> The Brown-Firth Research Laboratories, Sheffield, England.

*Mechanical properties at elevated temperatures*

Stability

Red hardness

Creep properties

*Mechanical properties at sub-normal temperatures**Resistance to corrosion and chemical attack* (including corrosion fatigue)*Resistance to scaling**Response to surface hardening*

Carburizing

Nitrogen hardening

Effect of various heat treatments on the above properties

Effect of various degrees of cold-work on the above properties

Effect of heat-treatment after cold work

*Additional data required from the standpoint of industrial application**Casting.* Feeding and production problems of heterogeneity*Hot-working.* Application to manipulation by forging, drop-stamping, rolling, and other processes*Heat-treatment.* Response*Machinability.* Feeds, speeds and tool angles*Cold-working.* Suitability to press work, stamping, punching, spinning, moulding, bending, beading, rolling, and drawing*Facility for welding**Response to pickling**Facility for brazing**Facility for hard and soft soldering.*

The following brief remarks may be made regarding the various laboratories in a physico-chemical establishment.

(a) **Main Laboratory.** This laboratory should be well lighted with windows, preferably on two or three sides. The room should be lofty, and from 40 to 60 square feet per worker should be allowed. A height of 12 feet is sufficient, but where high voltage work is carried out this should be increased. The lower figure applies more in the case of elementary courses and the latter for advanced workers on continuous work with more apparatus and experiments kept under control. It would not be advisable for more than thirty students to work in the same laboratory, and if a larger number has to be catered for at the same period, two or more rooms are generally to be preferred to a single large laboratory. For preference asphalt flooring should be adopted. In the Mellon Institute the aim has been to have a large number of compact laboratories (20'  $\times$  20' and 10'  $\times$  20') rather than enormous single laboratories such as are sometimes found in universities.

In the general design and lay-out the question of good ventilation should be kept in view. In physico-chemical work the need for fume cupboards with artificial ventilation is not so necessary as in general chemical work. Window ventilation is not always possible, and in these instances fans should be provided. When fume cupboards are necessary, the design should be such that ledges and sloping roofs are avoided since they are a source of dust. In the best designs the cupboards are sunk into the walls or the cupboard carried up as far as the ceiling. In some laboratories a current of air is drawn into the flues in the direction of the exit and the foul air continually removed from the

laboratory, fans driven by electric motors with rheostat controls being used to provide the draught. The use of purified air under pressure, as in the Plenum system, is adopted in some laboratories, while in large buildings the use of a shaft with a forced draught may be necessary. In the water mains through the laboratory low melting-point plugs should be fixed at required places in case of fire.

As indicated above, it is very important for the laboratory to receive as much natural light as possible. In addition, however, provision should be made to supply the so-called 'daylight'-effect lamps with special reflectors (e.g. the Holophane reflectors with prismatic glass shades, the contours of which are designed to give a predetermined distribution of light) for evening work or for special occasions. The lamps should be arranged so as to avoid excessive contrasts and glare. For laboratory work in physical chemistry it is considered that general illumination should not be less than 0.8 to 1 foot-candle (the foot-candle standard being the illumination received from a source of 1 candle-power falling perpendicularly on a surface at a distance of 1 foot). For particular operations a source of illumination up to 15 to 20 foot-candles should be available. In another successful system for the production of a 'daylight' effect, using electric light (Sheringham Daylight), the result is produced by the use of permanent pigments whose characteristic colour is due to their power of absorbing some coloured rays and reflecting others in such a manner that the colours towards the red end of the spectrum are largely absorbed, while those of the violet end are reflected. These pigments are arranged on the shade of the lamp so that a certain definite area of each colour is exposed to the light in such a manner and in such a proportion that the light reflected from the shade is an excellent substitute for a north-sky daylight. It is available for general lighting or preferably for the lighting of special benches while particular work requiring a uniform light is in progress.

Contrary to the general custom it is considered preferable, especially in advanced laboratories, to have as much bench space as possible round the walls so as to make the most of the window-lighting. This can be arranged more conveniently when the laboratory is long and narrow. Cupboards, combustion benches, ovens, movable tables and other equipment should be placed in the central space of the laboratory. In at least some of the more recently erected physico-chemical laboratories steam is now provided for heating, evaporation, distillation or general laboratory work. Where the laboratory is situated in a factory and steam is readily available advantage should be taken of the fact. In an isolated laboratory the case for the installation of a general steam plant is not so great. Electric current (alternating and direct)—with convenient plugs—water, gas, compressed air should also be available. A general vacuum supply is not recommended, but a portable vacuum pump, e.g. the Geryk or Lennox rotary, or a fixed Gaede pump (see Chapter IV, Section 5), is much more convenient and efficient. In this connection it must be remembered that the continual use of water-jet pumps in laboratories often involves a very large waste of water and fluctuation in pressure is often unavoidable. This is an argument in favour of a vacuum installation. All service pipes independent of appearance should be exposed, for convenience in repairs, &c.

The wall bench is generally to be preferred to the large double-sided bench in the centre of the room. The bench should be of simple design, and it is not recommended to close in the lower portion as a store cupboard. A height of about 3 feet and a width of 2 feet 3 inches will be found ample for most work. The gas taps should be workable from the outer edge of bench. The length will depend on circumstances. The top should be made of hard wood. Well-seasoned teak of a thickness of 1.5 inches has been found a very suitable wood from experience. Paraffin wax, linseed oil or beeswax and turpentine might be used to preserve the surface, but the general use of such impregnating materials is not recommended for a physico-chemical laboratory, as sometimes a slight stickiness on the surface may develop. Beechwood is a fair substitute for teak. Even cheap soft woods, if properly treated, may be employed without great disadvantage for the surface of laboratory benches. For this treatment a mixture of umber in turpentine, terebene ('drier') and raw linseed oil is used. The surface is later treated with melted beeswax or tallow mixed with turpentine and a hot iron is then pressed over the surface. The waxy surface is finally polished with a soft cloth. In America white-wood has been employed in some institutions and aniline black used for impregnation. The wood may also be treated as follows: The wood is soaked with an aqueous solution of aniline hydrochloride (15 per cent) and ammonium chloride (6 per cent). When thoroughly dry it is well washed with a strong aqueous solution of copper sulphate and potassium chlorate (8 per cent) and the two operations repeated two or three times. The boards are then washed with water and petroleum jelly rubbed into the surface. A dark-coloured bench-top results from this washing. This treatment, which is stated to harden the wood and make it less porous, is followed by washing with soap and then rubbing in raw linseed oil.

In a report issued by the Chemical Society, London, on laboratory furnishing, other materials have also been referred to, e.g. ferro-concrete (with rubber mats), plain deal covered with linoleum, and bench-tops of red tiles set on a light iron frame. Alberene stone—a type of Virginia soap stone—is largely used in America and volcanic stone in France.

A new table-top made of a porous non-warping ceramic substance, impregnated with bituminous substance, has been recommended. By heating under special conditions a coke-like material is formed in the pores, and an artificial cordierite slab is formed. It has very low thermal expansion, takes a high polish, resists abrasion and has good strength. It is not affected by solvents or rapid heating and cooling.

Bakelite laminated bench-tops and shelves are claimed to have special application in the modern laboratory. They are non-corrosive and unaffected by many chemicals. Laboratory units benches, &c., have been designed also in steel with a working surface coated with an acid-proof material or a stoving varnish. The whole unit is finished with a surface which is not affected by alkalis or acid fumes and is proof against corrosion and fire.<sup>1</sup>

For special work plate glass 0.25 inch to 0.375 inch thick, resting on rubber or on the wood bench, is sometimes employed.

Plate glass shelves on end supports are ideal for benches, but general equipment in this manner is very expensive. In the construction of general

<sup>1</sup> Van Dorn Process (N.Y.).

shelf accommodation wood is the most economical material to employ. For light apparatus and where no corrosive material is likely to come in contact with shelves the use of beaver board or other papier mâché substitute has been adopted in some laboratories. The type of cupboards, tables, stoves, &c., advisable to adopt will depend on circumstances and no general descriptions can be usefully specified.

The physico-chemical laboratory will require fewer sinks than the ordinary chemical laboratory. According to a conference arranged by the Chemical Society on laboratory equipment the opinion was in favour of glazed earthenware sinks and it was considered desirable to have a trap at the end of each block of benches to prevent the passage of solid waste into the main drainage channel. Except for the washing-up sink only comparatively small sinks should be needed, to carry away the water from condensers, filter pumps and such operations.

(b) **Extra Laboratories.** In first equipment the additional general laboratories should be sparingly fitted with permanently fixed benches, &c. Movable tables should be provided and electric and other power supplied should lead to fixed terminals in walls. For galvanometer and other work requiring freedom from vibration the erection of steady concrete blocks set into walls may be necessary.

(c) **Balance Room.** In an outline of a particular laboratory the authors arranged the balance room as a screened-off (with glass partitions) portion of the main laboratory. In other laboratories, especially in physico-chemical work, in contrast with general chemical work when fumes may be more prevalent, balances may often be kept in rooms where other work is carried on. Where, however, a special balance room is needed the following point should be kept in view.

The chief requirements of such a room are a uniform temperature, good lighting and freedom from draughts and direct sunshine. If the room is lighted from the north and the balances are placed along the south wall the light falls on the scale and enables it to be seen distinctly, while any radiation from outside falls equally on the two arms, and so is less likely to produce disturbing effects. It is a disadvantage to have the balance table against the outer wall, as in such an arrangement the disturbing effects due to bad weather are more pronounced. Double doors and windows are a distinct advantage. Since a rigid table is essential for accurate work the balance tables are best made entirely of reinforced concrete or of slate slabs supported on brick pillars built up from the floor. If the room is upstairs the supports can be built out from the wall.

(d) **Electrical Room.** The concentration of electrical work in one laboratory has the advantage of reducing the outlay in heavy electrical cables often necessary in modern investigation. Accumulators are stored in a small adjacent room. Switchboards may also be placed here.

In work on hydrogenation or with solvents the need for fireproof or flame-proof motors and switches in certain rooms arises, owing to the possible danger from explosion of gases and vapours. The Mond Research Laboratory, London, in the hydrogenation laboratory provide a standard alarm lamp somewhat similar to that used to detect coal-gas in mines. If a leak occurs in the hydrogen plant and the hydrogen in the air exceeds 1 per cent

the lamp operates a relay which automatically stops the machinery and activates a mechanism which causes a complete air circulation. With such a device the need for explosion proof motors is reduced.

(e) **Radioactive Room.** When radioactive work is carried out as part of the routine of the physico-chemical work, a special room is required for storage of radium and radioactive substances. This equipment is considered in the next section.

(f) **Constant-temperature Room.** In the outline scheme for a laboratory the constant-temperature room is generally shown with double walls and double doors. This room should also be efficiently ventilated and a fixed bench should be provided for thermostats. Usually the room is situated at the north side of the building. In one novel arrangement this room is situated in the centre of the main laboratory.

(g) **'Glass Workers' Room.** If possible it is of advantage to have a small room for glass-blowing work. The room should be free from draughts and the blow-pipe bench should be fixed away from the window as strong light is to be avoided on account of the difficulty in working with non-luminous flames in such light.

(h) **Dark Rooms.** In a smaller institution one moderately sized room would meet the general requirements of photographic work and occasional experimental work with polariscopes, spectrosopes, ultra-microscope, photometers, &c. In a larger physical chemical establishment there should be available one small room solely for photographic and general photo-chemical work, and a large room which could adequately be darkened as required. Photographic or colorimetric work might also require space. Efficient ventilation is necessary, especially when the room is occupied for long periods. With the ordinary type of ventilator some light may diffuse into the room and this point must be kept in view in arranging a suitable ventilating system. A lead-covered developing bench with a large sink will be found advantageous and good shelf space should be provided. Another good arrangement is a large sink covered with a wooden lattice on which work can be carried out directly. Water and electric light (as well as screened lamps for photographic work) should be available. Where photographic work or work of the type of matching colours, &c., in artificial light is in progress it is advisable for various reasons to have the room provided with double doors to prevent entrance of ordinary light with passage of people to and from the dark room.

(i) **Gas-analysis Room.** For this work a small laboratory would be suitable, and this should be fitted with suitable apparatus and reagents. Plugs for electrical supply are also a convenience. The temperature should be as near constant as possible. Good lighting is an advantage and if possible the windows should face in a northern direction. If an apparatus of the type of the Bone and Wheeler gas apparatus is often employed it is more convenient if it is mounted in the centre of the laboratory on a bench about 2 feet high. A high-pressure water supply and a sink will also be required convenient to the apparatus. It is well recognized that with the constant handling of mercury there is a definite risk of poisoning, and one feature to which particular attention should be paid in the construction of the gas apparatus is the elimination, where possible, of the necessity of

handling mercury, and the avoidance of methods which tend to splash the metal about the tray of the apparatus and over the floor of the laboratory. The floor of the laboratory should be covered with a composition which gives a smooth finish, easy to keep clean, and on which mercury does not collect in small crevices or tend to scatter in very fine particles. In this room mercury might also be stored and recovered.

(j) **Workshop.** This important section, which would be situated on the ground floor, need not occupy much space, but should contain a small vertical lathe, screw-cutting drill, carpenter's bench, a small hydraulic press, and various instrument-making tools. Such a shop will be of great assistance and may save loss of time in repairs of apparatus and plant and in providing for special new apparatus and equipment.

(k) **Library.** The scope and nature of the library will depend in the main to a certain extent on the nature of the physico-chemical problems dealt with in the laboratory. In addition to ordinary library service and card indexing of books, reports, &c., the need will often arise for efficient abstracting and distribution of information on one or more sections of physical chemistry, especially when systematic research work is being undertaken. This work will apply both to current literature and patents and may involve translation work.

## SECTION 2: THE RADIOACTIVITY ROOM

The parent body of many of the substances used as radioactive sources is radium. This radium is usually stored in solution, and the evolved emanation is removed and purified at intervals when sources are required for experimental purposes.

The radium should be stored in a room, or set of rooms, as far removed as possible from the laboratory in which it is proposed to carry out measurements and experiments, and all the operations involved in the preparation of the sources should be carried out in these rooms. The reason for this is twofold. Firstly, the presence of radiation from a large source makes it impossible to carry out measurements on weak preparations. Secondly, a certain slight escape of radon is inevitable. Owing to the long life of RaD, a long-lived contamination results of the walls of the room and objects in it, and careless handling of measuring instruments may result in their being rendered permanently useless.

The risk of contamination to the worker is high, and, whenever feasible, it should be adopted as a principle that the preparation of sources should not devolve on the person who desires to carry out the measurements. Exposure to the radiations is fraught with grave risks to the health of the operator, serious skin disorders such as dermatitis often resulting from careless handling and the neglect of various simple precautions. A full account of the physiological effects of these radiations is to be found in Meyer and Schweidler<sup>1</sup> and Curie,<sup>2</sup> to which the reader is referred for fuller information. For these reasons it is imperative that the worker should at all times be protected as far as possible from the radiations. Strong sources should be surrounded by several centimetres of lead, and during all manipulations the hands should be protected by surgical rubber gloves. The room should be well ventilated in order to reduce as far as possible the inevitable contamination, and secondly to minimize the risk of inhaling small quantities of radon which break down subsequently in the system. No time longer than is absolutely necessary should be spent in the radioactive room.

All the tools and implements which are likely to be needed should form an integral part of the furnishing of the room, and should not be removed from it on any pretext. Neglect of these essential precautions may easily lead to the contamination of a whole laboratory. While a full list of tools is largely a matter of personal taste, the following will usually be found essential:

Glass-blowing apparatus, blowpipe, glass-cutting knives, files, soldering tools, gas ring, solder and flux, rough files, sandpaper, matches, pliers, clippers, tweezers of various sizes, and an assortment of scissors. Other

<sup>1</sup> *Radioaktivität*, Teubner (Leipzig), 1926, pp. 259-64.

<sup>2</sup> *Radioactivité*, Hermann (Paris), 1934, Chap. XVIII.



objects which will be found of use are pencils and paper, and an old slide rule for carrying out calculations. Separate sets of tweezers and scissors should be kept for work on radium, actinium, and thorium sources.

A gamma-ray electroscope and stop-watch is often installed, but it is frequently rendered insensitive by the presence of a large natural leak due to radon contamination. Operations should, as far as possible, be carried out on paper sheets in order to reduce contamination of or from the benches. Suitable arrangements should be made for the removal and disposal of the soiled papers. A sink with a liberal supply of soap and abrasive powders and a fume cupboard for chemical operations complete the furnishing of such a room.

In order to facilitate the removal of the rubber gloves the hands should first be well dusted with talc, a liberal supply of which should always be available. The use of those proprietary preparations which dry to form a protective film which can afterwards be dissolved with soap should reduce the risk of contamination of the hands. Care should also be taken not to touch the outer surface in removing the gloves. The hands should be carefully cleaned before leaving the room and again on reaching the laboratory prior to handling any piece of apparatus.

## CHAPTER II

### BASIC MEASUREMENTS

#### SECTION 1: LENGTH

**INTRODUCTION.** Since practically all physico-chemical measurements can be expressed in terms of the fundamental units of length, mass and time, or their derivatives, such as area, volume or density, a short account is here given of these units and their derivation. In the study of electrical and thermal phenomena it is necessary to postulate two other fundamental units, such as specific inductive capacity and temperature, as the exact dimensions of certain of the quantities involved are unknown in terms of length, mass and time.

In some systems derivatives of the above fundamental units are taken as the standards and the latter derived from them. For example, force or energy is sometimes employed in place of mass.

**Units of Length.** The unit of length employed in physical chemistry is generally the metre, which is now an arbitrary standard and is known as The International Prototype Metre. It is the distance at the melting-point of ice at standard pressure between two marks on a bar of polished platinum-iridium of X-shaped section. This length has been accurately transferred to several similar bars from which in turn other copies have been made. The methods by which this has been accomplished are described later.

The metre standard is somewhat large for practical purposes, so it is divided into 100 equal parts called centimetres, which are in turn divided into 10 equal parts called millimetres. Still smaller units for X-ray and light-wave measurements are given by the Ångström or so-called 'tenth-metre' units, of which one hundred million ( $10^8$ ) equal one centimetre. The Ångström unit is generally written as Angstrom and is represented by the symbol Å. The millimicron, written  $1\text{ m}\mu$ , equalling  $10^{-6}$  mm., is employed for atomic and molecular dimensions. The micron, written  $1\ \mu$ , serves in the study of bacteria. There are 1,000 microns to the millimetre. Colloidal particles vary in size from  $5\text{ m}\mu$  to  $200\text{ m}\mu$ . This is approximately the range from the largest molecules to the lowest limit of microscopic definition. The metre has also been measured in terms of the wave-length of monochromatic light, using the interference apparatus of Michelson. The length of the standard metre was compared with the wave-lengths of monochromatic red, green and blue radiation, the spectrum of cadmium vapour being employed for the purpose. In one standard metre at  $15^\circ$  and 760 mm. pressure the number of wave-lengths was found to be

1,553,163.6 for the red radiation,  
 1,966,249.7 for the green radiation,  
 2,083,372.1 for the blue radiation.

This gives a method by which the metre standards could be recovered if necessary.

The connection between the metric and the Imperial system is shown by the following :

1 cm. = 0.3937 inches, or 1 inch = 2.54001 cm.

### MEASUREMENT OF LENGTH

The measurement of length is the most frequent and the most important of all physical measurements ; on it depends the working of a large variety of physical and physico-chemical instruments. The simplest and most obvious method of estimating a length is by its comparison with a scale divided into the units and sub-units in which it is to be determined. But the eye unaided can only judge approximately the coincidence between the ends of the length and the divisions of the scale, especially when it is impossible to bring the scale close to the terminal points ; e.g. determination of length of an irregular body. More accurate results can be obtained by providing a fixed caliper attached to the zero of the scale and a sliding caliper moving along the latter. All practical measurements depend on such transferences ; in the more accurate methods light is used to provide the calipers between the scale and the length, use being made of the fact that it travels in what appear to be straight lines. The methods and apparatus involved are described later.

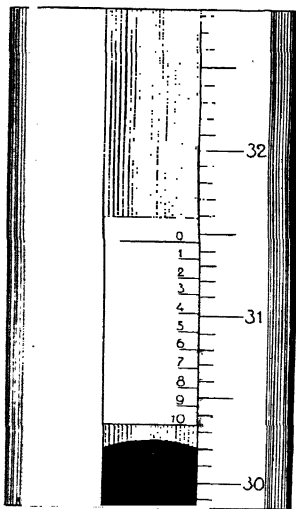


FIG. 1 (II)

**The Vernier.** Even when the length has been accurately transferred to the scale, one end opposite the zero of the latter, it will usually happen that the other end does not coincide with a sub-unit division of the scale. The sub-division on the scale may be increased, but sections less than a millimetre are not conveniently obtained. Great accuracy can, however, be secured by the use of a subsidiary scale called a 'vernier' which slides up and down past the main scale and is differently divided from it. There are two types of verniers—the barometer vernier (Fig. 1 (II)) and the sextant vernier (Fig. 2 (II)). On the former, if the main scale unit is divided into 10 smaller units, a length equal to 11 of these smaller divisions is marked off, and is divided into 10 equal parts, so that each of these latter then equals 1.1 small divisions of the main scale. To use the instrument, the zero of the vernier is laid as closely as possible to coincide with the extremity of the length under observation, the position of which is doubtful, and the number ( $n$ ) of the vernier division

which most nearly coincides with a scale division is noted. The vernier is numbered in a direction opposite to that of the main scale; counting back the vernier towards its zero the next division will be  $0.1$  of a small-scale division beyond the next scale division and the  $n$ th.  $0.n$  of a scale division beyond the  $n$ th scale division.

**The Sextant Vernier.** For decimal subdivision the unit here is equal to  $9$  of the small-scale divisions and each subdivision is equal to  $0.9$  scale divisions. This vernier reads in the same direction as the scale from the point of coincidence. In Fig. 2 (II) it is shown as employed for the measurement of angles in sexagesimal measure. The zero is  $0.n$  scale divisions short of the preceding scale division. To aid the eye in judging the various

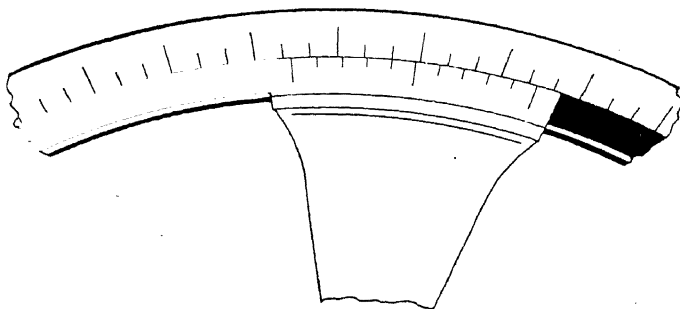


FIG. 2 (II)

coincidences a small magnifying-glass, or better a small microscope, is fixed to the vernier; this helps to avoid all parallax. We have here a simple example of the use of a ray of light as a caliper to which reference was made above. If there be no calipers on the scale the glass or microscope can also be employed to fix the coincidence of the zero of the scale and one extremity of the length.

**Parallax.** In all measurements in which the eye is used to estimate the coincidence of two objects, it is essential for correct results that the eye and the objects be in the one straight line. The error arising from neglect of this precaution is called the *error of parallax* or simply *parallax*. As it occurs in the use of a great variety of instruments this is a convenient place to refer to it. The collinearity necessary to avoid it may be assured in a variety of ways. The most usual consists in the use of a telescope or microscope; many examples of this are given. Or one may place a mirror behind the points to be compared with its plane perpendicular to the line joining these points. The object is then viewed so that the images of the latter are not seen. This is the principle involved in the magnetometer.

**Micrometer Screw Gauge.** The properties of the screw may be employed to obtain still smaller scale readings than is possible with the vernier. This is the principle involved in the micrometer screw gauge, which is much used in determining the diameter of wires and the like. Briefly it consists of a U-shaped piece of metal to one end of which is attached a fixed caliper; through the other end screws a movable caliper to meet the fixed

one ; the object to be measured is placed between the calipers. The position of the moving caliper is marked by a scale on a fixed hollow bar in which the moving piece screws. This scale is divided into half-millimetres and the screw has a similar pitch, so that one complete turn produces a movement of 0.5 mm. The edge of the rotating piece is divided into 50 equal parts ; hence a forward motion of 0.01 mm. can easily be observed. The difficulty of determining exactly when the end of the moving caliper is in contact with the body under investigation has been removed by completing an electric circuit when contact is made, whereby a current of 0.0002 amp. activates a telephone receiver. In the more elaborate forms of micrometer and other screw gauges the actual value of the dimension measured is shown directly on an indicator. This principle is capable of great expansion ; thus by using a screw with a large circle attached, the circumference of which is divided into 100 equal parts, and combining this with a vernier, differences of 0.001 of a millimetre can be determined. By gearing screws together by trains of toothed wheels as in a watch still further refinements are obtained. It is the screw which makes possible the dividing engine which can be employed not only to divide scales accurately into centimetres and millimetres, but also to rule diffraction gratings, the distances apart of the lines of which may be of the order of  $10^{-5}$  cm.

Other instruments may now briefly be described involving applications of the principles outlined.

**Spherometer.** This instrument, which is an application of the principle of the micrometer screw gauge, is applied chiefly to the measurement of the thickness of thin glass plates or to the determination of the radius of curvature of a spherical lens. In its simplest form it consists of a tripod with a screw carrying a graduated circle passing through the centre of the frame. This graduated circle is usually divided into 50 equal parts, and as the pitch of the screw is 0.5 mm. readings to 0.01 mm. may be obtained. In use the instrument is placed on a glass surface truly plane and the central screw adjusted so that the whole just tends to rock ; the screw is then touching the glass surface. The position of the top of the circle on the fixed scale, which is divided into millimetres, is noted, and the flat object to be measured introduced. The same procedure is carried out and a value for the thickness at once obtained.

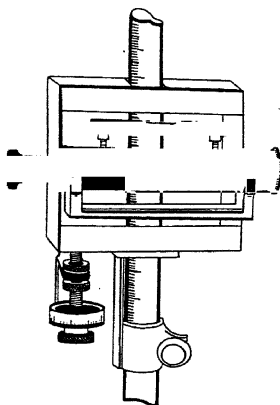


FIG. 3 (II)

**Cathetometer.** In the cathetometer (Fig. 3 (II) ), which is an instrument employed to measure vertical heights or lengths, coincidence is obtained by viewing the ends of the object through a telescope which slides on a bar adjusted to be exactly vertical. This adjustment is fixed by means of screws to its base, which is horizontal and carries spirit levels. In the eyepiece of the telescope are fixed a pair of spider threads or fine platinum wires, 'cross-hairs', at right angles to one another and placed so that they are visible simultaneously with the object viewed. In

order that this may be accomplished without strain on the eyes the telescope is first turned to a distant bright object, and the eyepiece adjusted so that the object is in focus, when the cross-hairs viewed by the other eye are also in focus. A scale is engraved on the vertical bar and the positions of a fixed mark on the telescope noted when the cross-hairs are exactly coincident with the images of the extremes of the distance under investigation. The scale should be made from an alloy having practically no temperature coefficient.

The instrument is especially useful in comparing the heights of mercury columns, &c. In accurate investigations a vernier is fixed to the telescope carrier and a small microscope employed to read it; allowance must then be made for the alteration in the length of the scale owing to the temperature at which the measurement is taken not being that of melting ice. In using the cathetometer it is of importance to bring it as near as practicable to the object to be measured, in order to minimize errors due to the axis of the telescope not remaining parallel to its original direction. Fig. 4 (II) makes this self-evident.

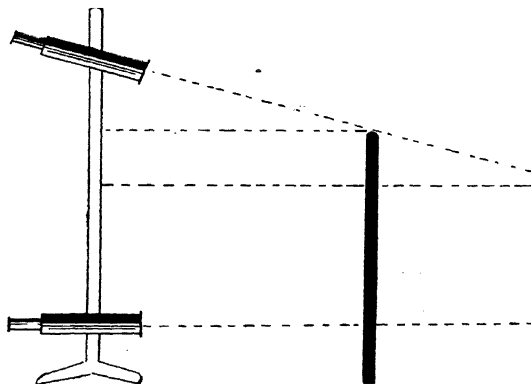


FIG. 4 (II)

A simple substitute for the cathetometer is described by Ramsay and Steele. A telescope is fixed opposite to a piece of mirror glass with a surface accurately plane. The glass can rotate about a horizontal axis; the amount of rotation necessary to bring the image of the extremities of the object into coincidence with the cross-hairs of the telescope is read off on an angular scale fitted with a vernier, and from this the length of an object, e.g. the height of a column of mercury, can be calculated to 0.01 mm.

**Travelling Microscope.** The simplest form of the travelling microscope is that of a horizontal cathetometer, a vertical microscope moving along a graduated horizontal bar, which is brought in turn over the ends of the length to be determined. Refinement is obtained by the use of a screw to move the microscope; this screw is graduated as with a micrometer screw gauge. This instrument gives exceedingly accurate results, but it can only be employed when the length of the object does not exceed a few centimetres.

**Measurement of Microscopic Objects.** The microscope may be employed to measure the length of a small object directly by fitting it with an eyepiece which contains a scale divided into equal parts. Fig. 5 (II) shows a micrometer eyepiece. The image of the object to be measured is compared with the image of the scale and the number of divisions that the required dimension equals is noted. The object is then replaced by a very finely divided scale, the size of which is known, and the number of divisions on the eyepiece scale corresponding to one division of the image on the known scale is observed. From these data the size of the object first viewed can be determined. Various modifications and refinements of this principle have been developed. Objects can also be measured by employing instruments with movable stages and movable eyepiece scales, the displacements of which can be determined by means of micrometer screw gauges.

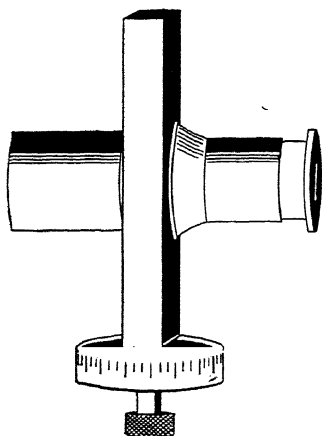


FIG. 5 (II)

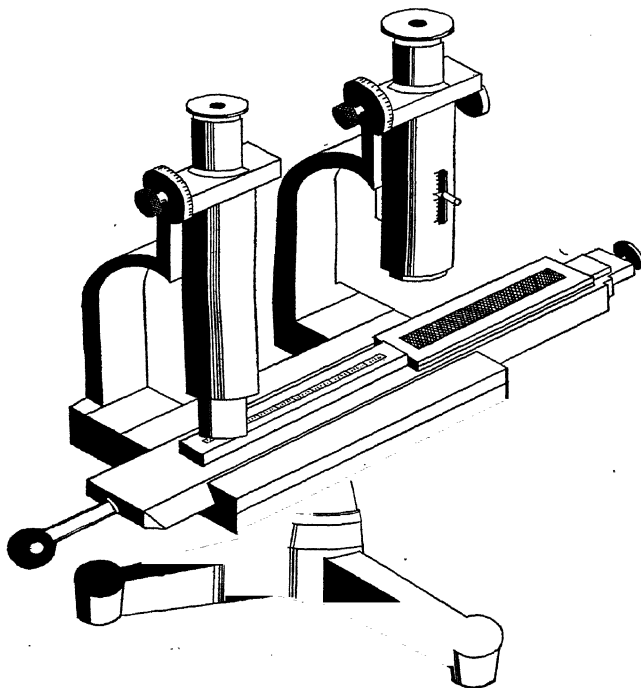


FIG. 6 (II)

**Comparator.** In the comparator (Fig. 6 (II) ) the travelling microscope is applied to compare nearly equal lengths, or to determine small changes in the length of an object, due to changes in temperature and the like. It consists of two travelling microscopes rigidly mounted at a fixed distance apart. The object to be measured is fastened so that its ends are almost beneath the microscopes and so that the line joining them is parallel to and vertically under that joining the centres of the object glasses of the microscopes, which must be placed as nearly vertical as possible. It is necessary that the length under examination should not differ by much from the distance between the microscopes. The latter are adjusted so that the cross-hairs in the eyepieces exactly coincide with the extremities of the length. The readings of the microscope scales are then noted. The object is replaced by a standard and the corresponding microscope readings obtained; the algebraic differences of the readings of the microscope scales enable the required length to be deduced immediately from that of the standard. It is by the use of the principle involved herein that the various fundamental standards of length are compared with their copies to within 0.001 mm.

**Interferometer.** The interference of two rays of monochromatic light from the same source, one of which has had to traverse a longer path than the other, produces interference bands which constitute a scale of half wave-lengths and may be applied to the measurement of very short distances. The accuracy is absolute to the 200th part of the wave-length of the light, which is an extraordinary figure considering that the greatest accuracy in measurements by mechanical means is of the order of the 25,000th part of an inch except in the generator comparator, with which measurements within one-millionth of an inch are claimed.

In the comparator in which this principle is applied homogeneous light of a definite wave-length is directed normally upon two or more parallel surfaces; the two reflected rays give rise to interference bands. One standard is mounted in the instrument and one of its dividing lines is adjusted under the spider line of a fixed microscope. A second travelling microscope carrying one of the plane glass surfaces is moved, so that its cross-hairs are fixed on the second defining mark of the standard. The second plane glass surface is rigidly fixed and the interference bands are examined in a properly constructed telescope. The first standard is now replaced by the standard to be compared and carefully adjusted so that its first defining mark is exactly under the spider line of the first microscope. If the second defining line is exactly under the spider line of the second microscope, then the two standards are exactly equal in length. If the above coincidence does not hold the microscope is moved by a very accurate screw until the spider line and the defining mark coincide. The distance travelled by the microscope is measured by counting the number of interference bands and the fractions of a band which pass the reference spot in the telescope, and multiplying that number by half the wave-length of the light employed.

**Measurement of Very Small Distances.** Such measurements are usually made employing some form of interferometer (see above). A method by which very small alterations in the length of a body can be determined depends on the recording of the induction effect produced on



a neighbouring circuit when the body changes in size. A method which is capable of measuring extremely minute distances is described by Whiddington.<sup>1</sup> He finds that if a circuit consisting of a parallel plate condenser and inductance be maintained in oscillation by means of a thermionic valve, a small change in the distance apart of the plates produces a change in the frequency and amplitude of the oscillation, which may be determined accurately by various methods. The name ultramicrometer has been suggested for the new instrument. This method has been developed by Dowling,<sup>2</sup> who has constructed a direct-reading ultramicrometer giving a sensitivity of reading corresponding to  $10^{-8}$  cm.

**Magnification Method.** A brief reference may here be made to a method differing somewhat in principle from those already discussed. It involves the projection with known magnification of an image of the dimensions under examination on a screen. This image is then measured, using an appropriate instrument. An interesting application of this method was employed by Barratt<sup>3</sup> to compare the lengths and diameters of different types of fibres, using a magnification of 16.2 diameters for the fibre lengths, and 880 for the fibre diameters.

The principle has a converse application in the production of finely divided scales for microscopic work by the photographic reduction of suitable larger scales. Photoelectric methods have been also applied.

The more important length-measuring instruments employed in physical chemistry have now been described. For a detailed description and other applications of the principles involved, together with an account of the precautions and corrections necessary in their use, the original literature should be consulted. The errors due to the refraction of the light through the material composing the tubes are avoided by immersing the tubes in a liquid of the same refractive index as the glass, or by carrying out the measurements by means of X-ray shadowgraphs.

<sup>1</sup> *Phil. Mag.*, 1920, 40, 634.

<sup>2</sup> *Sci. Proc. Roy. Dubl. Soc.*, 1921, XVI, 18, 185.

<sup>3</sup> *J. Text. Inst.*, 1922, 13, 3.

## SECTION 2: ANGULAR MEASUREMENT

**Units of Angular Measurement.** The unit of measurement for angles is the radian which is equal to the angle subtended at the centre of a circle by an arc of the circumference equal in length to the radius. The number of radians in an angle is said to be its circular measure. The radian as a unit is, however, of theoretical rather than practical interest; the practical unit in which all measuring instruments are graduated is the degree, of which there are 360 to a complete rotation. This unit is indicated by the symbol  $^{\circ}$ ; it is divided into sixty equal parts called minutes, written  $'$ ; a minute is in turn divided into sixty equal parts called seconds, written  $''$  (cf. the sexagesimal divisions, also employed in measuring time).

From these definitions the following relations at once follow:  $\pi$  radians  $= 180^{\circ}$  where  $\pi$  signifies the ratio of the circumference of a circle to its diameter and is equal to 3.14159265. . . . Also  $1^{\circ} = 0.017453$  radians. It is of interest to note that an angle is measured as a pure ratio and has the dimensions zero with reference to all the fundamental units.

In the measurement of solid angles the area of the surface of a sphere subtended by the angle from the centre of the sphere is divided by the radius of the sphere squared. The quotient is the measure required.

**The Measurement of Angles.** As will be clear from the above discussion of length-measuring instruments the measurement of angles is also a frequent operation. The method most usually employed is one of direct comparison. This is provided by a protractor, i.e. a circle or scale graduated in degrees and its subdivisions; how far the subdivision is carried depends on the size of the circle and the accuracy required; by the aid of a vernier, readings to ten seconds can be obtained without the necessity of an inconveniently large circle. The position of a pointer rotating about an axis through the centre of the circle can also be observed, preferably by means of a microscope. A large number of corrections must be applied in readings of great accuracy. In many instruments various properties of light are employed to allow of the value of an angle being deduced. Chief among these is the sextant, but as it is rarely used in physical chemistry the reader should refer to a textbook of physics for an account of it if necessary. Other instruments in which light gives a measure of an angle, such as the mirror galvanometer, will also be found described there. In Chapter XII, Section 7, the employment of a similar method of measuring an angle to determine a length is discussed.

The spirit level can be applied to measure the angle between any given surface and the horizontal. For an account of the method employed a book on civil engineering should be consulted, which will also contain an account of the theodolite, which, although an accurate instrument for measuring angles, finds little application in physical chemistry.

In crystallography the determination of the angles between the surfaces of a crystal is of importance, and a special instrument, called the goniometer, is employed to measure them. A description of this instrument will be found in the next section.

**Units of Area.** The units of area are based directly on the units of length, thus we have the square metre = 1 m.<sup>2</sup>; the square centimetre = 1 cm.<sup>2</sup>, &c.

**The Measurement of Area.** The measurement of area is not a frequent operation in physical chemistry; the necessity for it arises, e.g. when determining current density, for which the surface of an electrode must be known. The problem also occurs in measuring radiation densities. Surfaces of a definite geometrical shape can be estimated from a number of linear measurements by calculation; this method can be extended to all linear surfaces making use of Simpson's Rule. Another method (an approximate one only) which may sometimes be applied involves the cutting of a piece of good, moderately stiff paper to the shape of the surface and weighing it. The weight of a known area of the paper is also determined when a simple calculation gives the area required. Alternatively, the area may be found by drawing the figure to scale on squared paper and calculating the value required from the number of squares covered by the figure. When these methods fail a plane area can always be measured by means of the Amsler planimeter. Areas which extend in three dimensions must be obtained by calculation, for example, by mathematical approximation. Here it is impossible to lay down any general rule; each case must be considered on its merits; where a surface is capable of being developed on a plane surface this operation should be carried out and the area at once be obtained.

### SECTION 3 : CRYSTAL MEASUREMENT

**Crystal Forms.** The crystal is a regular solid of definite form enclosed by four or more faces. The regular form of a crystal is due to the regular arrangement of the molecules of which the substance is built up. The regularity is that of a three-dimensional pattern in which a certain unit of structure is repeated over and over again in space. This theory has been held for a good many years, but it is only comparatively recently that with the aid of X-Rays the actual nature of the unit of the pattern of the crystal was established (see chapter on X-Ray Spectroscopy). Where two faces of a crystal meet they form an 'edge'; this is the line of intersection of the planes of the faces. The angle between two such planes is called the 'interfacial angle'.

Fig. 7 (II). (a) represents a crystal of quartz ; it shows some of the ' faces '



FIG. 7 (II)

and edges. A horizontal cross-section through the middle of this crystal would give a regular hexagon.

This figure represents a regular crystal of quartz. There are also found quartz crystals which have quite a different shape. These variations affect the relative size of one or other of the faces, but the interfacial angles are always the same. We may get a crystal of quartz like Fig. 7 (II) (b), a cross-section of which gives a hexagon with one pair of opposite sides longer than the others. Its angles are identical with those of a regular hexagon. The relative sizes of the faces developed in the two crystals are different, although their interfacial angles are similar.

In a crystal there are generally three, four or more interfacial edges parallel to each other. The series of faces making these edges is called a 'Zone'.

**Preparation of Crystals.** The general solvent used for the preparation of crystals is water, but sometimes a solvent like alcohol, benzene, carbon tetrachloride, &c., gives better results, as the substance whose crystals are required may not be soluble except in one of these. It is noticed that substances generally are soluble in liquids which have a structural resemblance

to them ; for instance, hydroxy compounds in water and alcohol, and hydrocarbons in another hydrocarbon like benzene.

For the investigation of crystals, the chemist must prepare both a pure sample of the substance and good crystals. Crystallization of a substance generally purifies it, and if carefully carried out gives good specimens. The best method of preparing well-formed crystals is by making a hot and nearly saturated solution of the solid in a good solvent, at a temperature not much above that of the surrounding air. The solution is then filtered into a flat-bottomed vessel to about an inch from the bottom, the vessel having previously been warmed. The solution should then be placed on a piece of non-conducting material such as flannel, in a cupboard, free from draughts, and allowed to stand for some time. All dust particles should be excluded from the vessel. With aqueous solutions, they may be placed with advantage in a large desiccator. The solution cools and loses some of the solvent through evaporation, and thus crystals of the substance separate out. This method cannot be used in the case of substances more soluble in the cold than in hot solutions, e.g. calcium citrate.

The crystals which come out in this way are well-defined and fairly large, and can be dried with filter-paper by moving the crystal around on it with another piece of filter-paper. If the crystals obtained are not of sufficient size they can be allowed to grow. One of the best of the sample is taken and placed in a vessel containing a saturated solution of the substance and allowed to remain there. Evaporation goes on and the crystal builds itself up. This growing can be continued by removing and drying the crystal, adding to the solution a few mls. of hot supersaturated solution and replacing the crystal. In order to obtain uniform growth, a different face of the crystal is placed on the bottom each time. Large well-defined crystals suitable for examination are thus obtained. With very volatile solvents, e.g. carbon disulphide, the saturated solution should be allowed to stand in a vessel with a cover containing a number of small holes. This will reduce rate of evaporation and well-defined crystals have a better chance of forming.

A good method of keeping the crystal is to put a small spot of wax on a crystal face and allow the point of a heated pin which has been put through the centre of a cork to touch it. The crystal sticks to the pin and the cork is put into a specimen tube, keeping the crystal from touching the sides.

**Measurement of Crystal Angles—Goniometers.** Since it is not

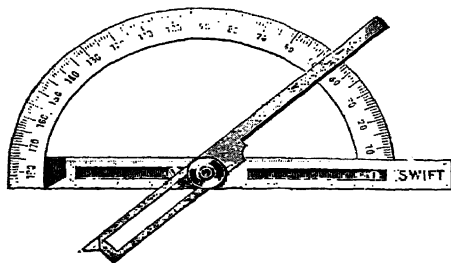


FIG. 8 (II)

diameter and graded in degrees (Fig. 8 (II)).

the sizes of the faces but the interfacial angles that are constant for a crystal of any substance, it is very important that we should have instruments to measure the crystal angles. As long ago as 1780 a 'contact goniometer' was invented by Rome de L'Isle and his assistant, Carangot, for this purpose. It consists of a semicircular lamina, about 3 inches in

The crystal is placed at the centre, with one face on the base line, and the arm is brought to touch the other face. The reading given by this arm is the interfacial angle. This instrument is not very accurate but for a long time it helped greatly in increasing the knowledge of crystals.

**Reflection Goniometers.** When the reflecting goniometer was invented in 1809 by Wollaston great progress was made in Crystallography, as the angles of crystals could now be determined with great accuracy and small crystals could also be examined. All modern reflection goniometers are elaborate forms of this instrument. The principle underlying all such goniometers is that a crystal face will reflect a beam of light. The position of the reflected ray can be noted. If now the crystal is rotated around the crystal edge between this face and the next one till the latter comes into the position of the first one, the reflected ray will be in exactly the same position as it was originally, except that now it is reflected from the second face. The angle through which the crystal has been rotated is the angle between the normals to both faces or is the supplement of the interfacial angle.

**Mier-Wollaston Goniometer.** This instrument is on the lines of the original Wollaston goniometer, but developed in accordance with the designs of Miers. For this instrument no telescope or collimator is used to get the position of the ray of light. The principle is that when a crystal is placed over a mirror and a ray of light from a distant signal slit is let fall on the crystal face the image of the slit is seen in the face. If the face of the crystal is not parallel to the plane of the mirror two images are seen, the second one being the reflection in the mirror. When the crystal face is parallel to the

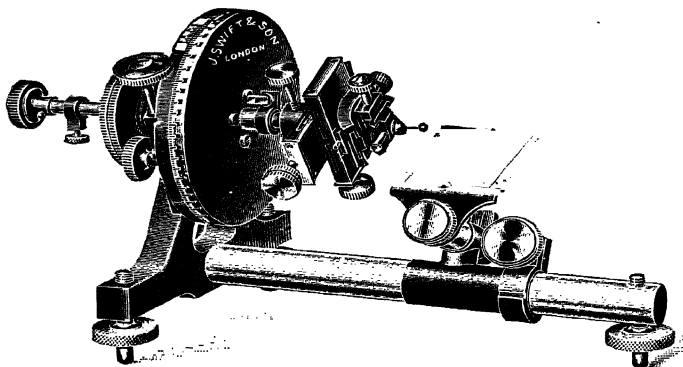


FIG. 9 (II)

mirror only one image is seen. This is a very accurate method of obtaining parallelism between the mirror and the crystal face. When this is obtained the crystal is rotated round one of its interfacial edges till the next face is got parallel to the mirror. The angle through which the crystal has been rotated gives the supplement of the interfacial angle.

The crystal is fixed above the mirror (Fig. 9 (II)), and can be centred by means of screws (centring means that it can be made to rotate round the central horizontal axis of the instrument). The circle is about 5 inches in

diameter and is divided into half degrees. The vernier gives readings to 1 minute ( $1'$ ). The crystal is rotated by a screw having a fine adjustment. The mirror can be adjusted by means of screws so that it is parallel to the axis of the goniometer. The source of light is a narrow slit in a window. The crystal is rotated till the two images are coincident, then the reading of the vernier is taken and the crystal rotated again till the next face is parallel to the mirror. The difference in the readings gives the supplement of the interfacial angle. All interfacial angles in a zone can be found by the one setting. The angles in the other zones can be got by resetting the crystal.

In this goniometer a collimator and telescope can be used in place of the mirror, as in the next type of instrument.

**Large Horizontal Circle Goniometer.** This is different from the Wollaston vertical circle goniometer in that the circle here is horizontal. It has advantages over the former apparatus in that it allows more rigid holding of the crystal and it can also be used for measuring refractive indices.

The collimator (Fig. 10 (II) ) is fixed rigid to one of the legs. The telescope, movable around the divided circle, is attached to the outer circle and

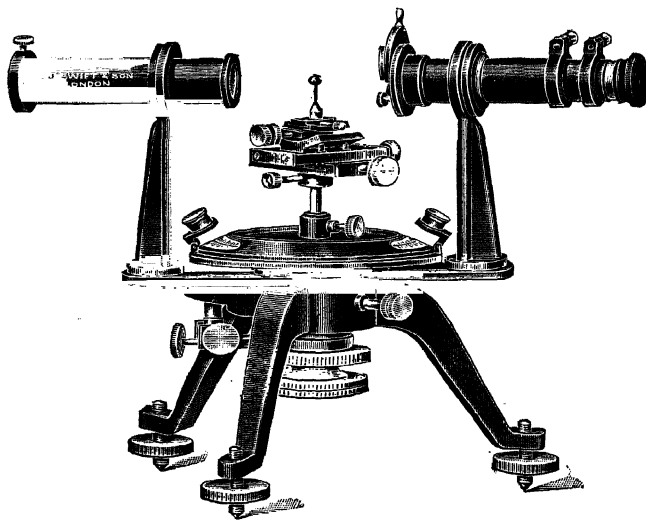


FIG. 10 (II)

carries two verniers. The circle has a radius of 6 inches and is graduated directly to 15 minutes. The verniers give readings to 30 seconds. The crystal is mounted on a pin and can be made to move with the inner divided circle. The crystal can be centred by means of screws. The crystal may be rotated independent of the inner circle by another screw. When the crystal is centred the telescope is moved round till the reflection of the slit in the collimator is focussed accurately on the cross wires. The telescope is then fixed. The reading on the vernier is taken and the crystal and inner circle rotated together till the next face reflects the image of the slit on the cross

wires. The vernier reading is again taken and the difference in readings gives the supplement of the interfacial angle. As with the preceding instrument all the angles in one zone can be got with one setting of the crystal.

**Crystal Grinding Apparatus.** Sometimes it is desirable to have a face on a crystal planed and smoothed or it may be required to make a crystal with definite angles (for use in X-Ray work). This can be done by means of the Crystal Grinding apparatus (Fig. 11 (II)). The type shown was designed by Dr. H. H. Thomas, F.R.S., and W. C. Smith and consists of a triangular metal plate B traversed by three steel screws S, one of which carries a graduated head. The pitch of this screw is such that one revolution tilts the axis of the instrument  $0.5^\circ$ . On the vertical axis is a solid metal cylinder P capable of vertical movement and of rotation in a graduated collar D. The screw can stop the rotation without interfering with the vertical motion. Drilled holes are made in the lower end of the cylinder to hold chucks and crystal holders. By the use of chucks and the graduated screw (s) a face of any desired angle can be cut and polished on a crystal.<sup>1</sup>

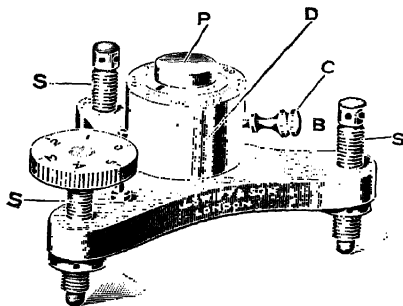


FIG. 11 (II)

**Symmetry.** All known crystals can be classified under one or other of the seven systems or classes. The crystals differ from one another in regard to the relative lengths and angles of intersection of the axes and consequently in their symmetry and their interfacial angles.

There are three kinds of symmetry: (1) axes of symmetry; (2) planes of symmetry; (3) centres of symmetry.

(1) Axes of symmetry. These are divided into:

- (a) Digonal or Diad Axis. One round which, if a body is rotated through  $180^\circ$ , the position is the same as at the start except a different face is in the place of the original one. In a cube there are six such axes (diagonals joining opposite corners and lines through the middle points of opposite sides).
- (b) Tetragonal or Tetrad axis is one such that every consecutive rotation of the body through  $90^\circ$  round this axis puts the body in an exactly similar position as at the start. In a cube there are three such axes.
- (c) Trigonal or Triad Axis. Rotation round this axis through  $120^\circ$  gives original position.
- (d) Hexagonal or Hexad Axis. In this case rotation through  $60^\circ$  gives original position.

(2) A plane of symmetry is such a plane that the structure on one side bears to that on the other the same relation as object and image.

(3) A centre of symmetry is a point in a body such that any line drawn

<sup>1</sup> The electros for Figs. 8 (II) to 11 (II) were supplied by the manufacturers, Messrs. J. Swift & Sons, Ltd., London.



through it and terminated by the surface of the body will be bisected at the point.

**The Seven Systems of Crystals.** From the elements of symmetry given it has been proved that there are thirty-two possible classes of crystals, each determined by a certain combination of symmetry elements. All crystals so far examined belong to one or other of these classes and examples of nearly all the possible classes have been found among actual crystals. The thirty-two classes are grouped into seven systems. The class in each system which possesses the highest symmetry is called the 'Holohedral Class'. The 'Hemihedral Class' is one where degradation of symmetry suppresses half the number of possible faces. The 'Tetartohedral Class' is where three-quarters of the faces are suppressed. 'Hemimorphic Class' is a special type of Hemihedral class. The following description of the Seven Systems has been outlined by R. Molloy:

I. *Cubic or Regular System* (Figs. 12 (II)–14 (II)). This system has three equal imaginary crystal axes at right angles to each other. It has five classes—

- (a) Holohedral Class has twenty-two elements of symmetry, i.e. thirteen axes of symmetry and nine planes. The axes are three tetragonal, four trigonal and six diad axes.
- (b) Gyroidal hemihedral.
- (c) Pentagonal hemihedral.
- (d) Tetragonal hemihedral.
- (e) Tetartohedral.

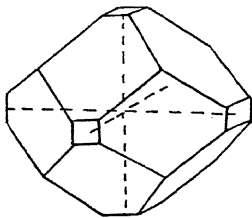


FIG. 12 (II)

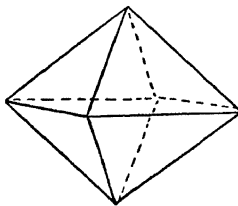


FIG. 13 (II)

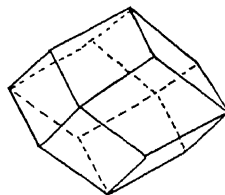


FIG. 14 (II)

In all the lower classes certain elements of symmetry in the Holohedral class disappear, but the three tetragonal axes are always present.

Examples of this system are alum, magnetite, sodium chloride, potassium chloride, barium nitrate, galena, lead nitrate, silver chloride, arsenic trioxide, diamond, fluorspar, potash alum and chrome alum.

II. *Tetragonal System* (Fig. 15 (II)). The crystals belonging to this system have three axes at right angles. Two of these are equal. The unequal axis is the principal one and has digonal symmetry in every class belonging to this system. In the Holohedral there are also four diagonal axes at right angles to the principal one, also five planes of symmetry, four of which intersect in the principal axis, the other one being perpendicular to it. There are seven classes in this system.

Examples: Zircon, potassium bi-sulphate, potassium ferrocyanide,

rutile, tin, mercuric cyanide, mercurous chloride, potassium dihydrogen phosphate, strychnine sulphate and potassium hydrogen arsenate.

III. *Ortho-Rhombic or Rhombic System* (Fig. 16 (II), 17 (II)). This system is referred to three rectangular axes, all unequal. The Holohedral class has three diagonal axes of symmetry. There are three planes and a centre of symmetry. This system has three classes: Holohedral, Hemihedral and Hemimorphic.

Examples of this system are sulphur, zinc sulphate, barytes, potassium sulphate, magnesium sulphate, potassium permanganate, iodine, silver nitrate, sodium arsenate, silver sulphide, lead carbonate, sodium phosphate, potassium chlorate, and potassium chromate.

IV. *Hexagonal System* (Fig. 18 (II)). Crystals belonging to this system have four axes; three of them are inclined at  $60^\circ$  to one another in the same plane and are equal in length. The fourth is at right

FIG. 15 (II)

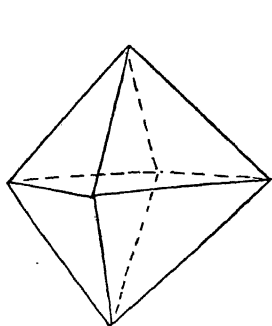


FIG. 16 (II)

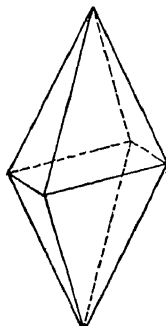


FIG. 17 (II)

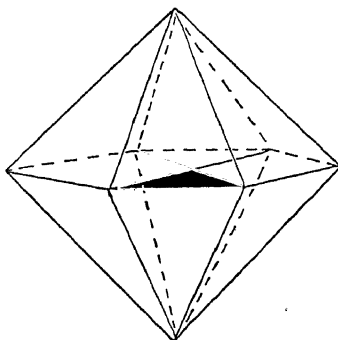


FIG. 18 (II)

angles to the others, and is unequal to them. The three axes have diagonal symmetry and the principal axis sixfold. There are five classes.

Examples are witherite, beryl, apatite, copper sulphide, lead iodide, magnesium, zinc, cadmium, cadmium sulphide, calcium, strontium antimonyl tartrate, and greenockite.

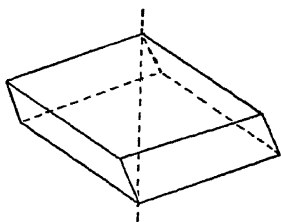


FIG. 19 (II)

V. *Rhombohedral or Trigonal Symmetry* (Fig. 19 (II)). This system comprises seven classes. They are sometimes included under the Hexagonal system, the principal axis having degraded from sixfold to trigonal symmetry. This system is sometimes referred to the axes of the Hexagonal system or better to three equal and

equally inclined axes, but the angle is not  $90^\circ$  except on rare occasions. Examples are quartz, calcite, tourmaline, calcium chloride ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), zinc carbonate, ferrous carbonate, manganese carbonate, graphite, and sodium nitrate.

VI. *The Monosymmetric, Oblique, or Monoclinic System* (Fig. 20 (II)). Crystals of this system are referred to three imaginary axes of unequal length, two of them being inclined, at an oblique angle, and the third being perpendicular to the plane of the other two. This system has three classes: Holohedral, Hemihedral, and Hemimorphic. The Holohedral class has a plane of symmetry containing the two obliquely inclined axes and a digonal axis of symmetry perpendicular to that plane.

Examples: Ferrous sulphate, borax, cane sugar, sodium carbonate

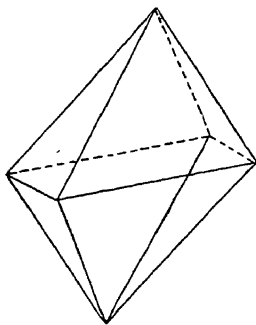


FIG. 20 (II)



FIG. 21 (II)

( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), sulphur (from fusion), arsenic disulphide, potassium chlorate, tartaric acid, and realgar.

VII. *The Asymmetric, Anorthic or Triclinic System* (Fig. 21 (II)). This system is referred to three unequal and unequally inclined axes. It has two classes. The Holohedral class has a point of symmetry so that every face has a parallel fellow. The Hemihedral Class has no symmetry and no parallel faces.

Examples are copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), potassium dichromate, grape sugar, boric acid, copper selenate, potassium ferricyanide, and calcium thiosulphate.

**Description of Crystals.** From the rules of symmetry it might be inferred that any plane obeying these laws as regards mode of repetition might be possible, but only very few planes inclined at certain definite angles repeated in accordance with symmetry are actually found developed. This simplicity shows that the crystal is a homogeneous structure composed of definite structural units of tangible size, probably the chemical molecules, built upon one of the space lattices shown by Bravais. To understand this law we must show how a crystallographer describes a crystal, i.e. labels its numerous faces.

Any point in space is defined by reference to three planes. In the simplest case these are at right angles, and intersect in three rectangular axes X, Y, Z, Z being vertical, Y lateral, and X back and front. The co-ordinates of any point define its position. We can imagine three such axes inside a crystal. From these any point on a crystal face, as well as the crystal face itself, can be defined (as the crystal face will cut each of the three axes). The axes chosen are the directions of the intersections of the three

best developed faces. In the case of the Cubic, Tetragonal, and Rhombic systems these axes will be at right angles. The edges of the cube, tetragonal, and rectangular rhombic prism will be the axes, and we can imagine these moved into the centre of the crystal. In the Monoclinic two of these axes will be at right angles and the other will not. In the Triclinic system no two of them are perpendicular. In the Hexagonal system there are four axes, one perpendicular to the other three which meet at an angle of  $120^\circ$ . In the Trigonal, except in rare occasions, they are not at right angles. In all cases, except those of the Cubic and Trigonal systems in which the axes are equal, a method of determining the relative lengths of the axes must be found. This is obtained by choosing a fourth important face inclined to all the three axes or if no such one is obtainable by getting two other well-developed faces each inclined to two of the axes and measuring the lengths these faces cut off on the axes. When both the crystallographic axes and their lengths are found we see on examining all the other faces that they cut off lengths from the axes represented by low numbers 2, 3, 4 or 5. By far the greater number of faces do not cut more than three unit lengths from any axis ('The Law of Rational Indices').

**Crystal Notation.** A system of notation was introduced by Miller in 1839. If  $m$ ,  $n$ , and  $r$  be the three numbers expressing the three intercepts cut off by a face on the three axes,  $x$ ,  $y$ , and  $z$ , and if the Millerian index be  $h$ ,  $k$ , and  $l$ , then  $h = \frac{x}{m}$ ,  $k = \frac{y}{n}$  and  $l = \frac{z}{r}$ . If the symbols stand for one particular face they are expressed  $(h, k, l)$ , and if they represent a whole set of similar faces they are written  $\{h, k, l\}$ . For an actual example, suppose a face, not a primary one (one used to obtain the lengths of the axes), makes intercepts 2, 3, 6, then  $h = \frac{x}{2}$ ,  $k = \frac{y}{3}$ ,  $l = \frac{z}{6}$ . In the case of the cubic crystal where  $x = y = z = 1$ ,  $h = \frac{1}{2}$ ,  $k = \frac{1}{3}$ ,  $l = \frac{1}{6}$ , or, to bring these to whole numbers,  $h = 3$ ,  $k = 2$ ,  $l = 1$ . That particular face is then represented by  $(3, 2, 1)$ . If the three intercepts were cut from the negative sides of the three axes the face would be  $(\bar{3}, \bar{2}, \bar{1})$ . For the whole set of similar faces we have  $\{3, 2, 1\}$ , which would represent the following eight faces:  $(3, 2, 1)$ ,  $(\bar{3}, \bar{2}, \bar{1})$ ,  $(3, 2, \bar{1})$ ,  $(\bar{3}, \bar{2}, 1)$ ,  $(3, \bar{2}, 1)$ ,  $(\bar{3}, 2, \bar{1})$ ,  $(3, 2, 1)$ ,  $(\bar{3}, \bar{2}, \bar{1})$ .

## SECTION 4: VOLUME

**Absolute Units.** The unit of volume from a purely theoretical standpoint should be based on the unit of length. In the metric system, however, the unit of volume known as the 'litre' is fixed otherwise. It is defined as the space occupied by a mass of 1 kilogram of pure water at its temperature of maximum density (about 4°) and at normal pressure (760 mm. of mercury at 0°). Originally, it was intended that the theoretically desirable relation should hold, and that the litre should be equal to 1,000 c.c. exactly where 1 c.c. is regarded as the volume of a cube 1 cm. long, 1 cm. wide, and 1 cm. deep. Later determinations, however, have shown that, actually, the litre is equal to 1,000,028 such cubes. As a result, the millilitre (ml.), or thousandth part of a litre, and the cubic centimetre are separate and distinct units of volume unconnected by any simple physical relation, a fact which is sometimes overlooked. The Bureau of Standards in Washington formerly graduated vessels in cubic centimetres 1,000 to the litre; such cubic centimetres strictly can be regarded only as  $\frac{1}{1,000}$  of the litre and not as cubic centimetres. For ordinary laboratory purposes the differences involved are negligible, being approximately 0.003 per cent.

The policy of the Bureau of Standards is indicated by the following extract from a Circular of the Bureau. 'In all volumetric work the unit of volume employed is the millilitre and not the cubic centimetre, but in this country (America) it is often designated by the letters "c.c." This designation has been used in former editions of this circular, but beginning with this issue the more correct designation "ml." will be employed. For the present, apparatus inscribed "c.c." will not be rejected for that cause alone, but it is expected that manufacturers will use the designation "ml." exclusively as soon as practicable.'

The Chemical Divisional Council of the British Standards Institution appointed in 1932 a Technical Committee for the Standardization of Scientific Glassware and Laboratory Ware. The National Physical Laboratory has co-operated closely with the working of this committee and a number of British Standard Specifications for scientific glassware have been issued.

In 1933 a *Report on Metric Units of Volume*, No. 501, 1933, was published by the British Standards Institution. In this report it is stated: '... the millilitre has been adopted as the unit in terms of which British Standard volumetric glassware shall be calibrated, and as the unit to be employed in the description of analytical methods'. This report has also been endorsed by the Australian Standards Association (Australian Standard K.58—1936).

The whole of the volumetric glassware submitted to the National Physical Laboratory for test continues to be calibrated in terms of the millilitre and marked 'ml.' by the manufacturers. The use of the millilitre and "ml." in literature is increasing.

It may be pointed out, however, that the density of even highly purified waters may vary appreciably owing to the presence of 'heavy water'. The difference between the millilitre and the cubic centimetre is of the same order of magnitude as the differences that may be obtained in waters of different 'heavy water' content.

In this chapter the term 'ml.' is used instead of 'c.c.' and later it is intended for uniformity to eliminate the symbol 'c.c.' entirely.

The relation between the metric and the Imperial system of measuring volumes is shown by the following:

1 cubic inch	= 16.3865 ml.
1 cubic foot	= 23.317 litres.
1 gallon (Imperial)	= 4.54596 litres = 277.421 cubic inches.
1 U.S. gallon	= 0.83268 Imperial gallon.

**Mohr's Units.** Previously volumetric chemical apparatus was graduated on the Mohr system, in which the unit is the volume occupied by a quantity of pure water which, when weighed in air at a standard temperature (17.5°) and at 760 mm. of mercury pressure, and with a content of moisture and carbon dioxide such that its density is 0.0012 grams/ml. against brass weights of density 8.4 grams/ml., has an apparent weight of 1 gram. On this basis for a standard temperature of 15° the volume corresponding with 1,000 Mohr grams is 1,001.980 c.c.

In a report issued by the Joint Committee for the Standardization of Scientific Glassware in August 1924 the litre and millilitre are recommended as the standard units of volume. A temporary recognition of Mohr's system is suggested. The unit recommended is the G.W.A. (grammes of water in air), and it is defined as 1,000 G.W.A. = 1,002 ml., so that it is at room temperature practically identical with the old Mohr unit, and conversion to millilitres and vice versa is readily accomplished.

In volumetric chemical analysis Mohr's method of graduation gives rise to no error because here the volume measurements are only relative. It is therefore of no consequence what volume is taken as the unit, provided the same unit is employed throughout. When, however, apparatus is to be used in the preparation of solutions of a definite concentration, or for similar purposes, that apparatus must be graduated in true millilitres.

## MEASUREMENT OF VOLUME

This is, especially for liquids, one of the most frequent operations in practical physical chemistry, and as a great number of methods have been developed the subject is best considered for the three states of matter separately.

**Solids.** The volumes of certain regularly shaped solids may be obtained from linear measurements, applying appropriate mathematical laws. Of solids generally the volume is determined by weighing, and dividing the weight by the density. A volume determination is of course necessary for the estimation of the density, but a regularly shaped piece of the material, if available, may sometimes here be employed. Displacement methods in which the solid volume is replaced by a liquid or gaseous volume, which is then measured, are, however, more usual. For instance, a vessel is com-

pletely filled with a liquid in which the solid under investigation is insoluble ; the latter is immersed in the liquid and the quantity of the latter displaced measured in a graduated vessel, or the volume determined by weighing. (See determination of the volume of a liquid below.) Alternatively the liquid may originally be placed in a graduated vessel and the change in the indicated volume on the addition of the solid noted. The subject is further discussed in the chapter on density.

A mercury displacement volumeter has been described by Jackson,<sup>1</sup> which, with certain modifications, is very suitable for the measurement of the volume of solids. The type described below is designed for the measurement of the volume of narrow rods (Fig. 22 (II) ). A piece of plate glass, C, is pressed against the ground end of the glass tube E by a rounded wooden button B on the end of a spring-loaded lever. By depressing the other end

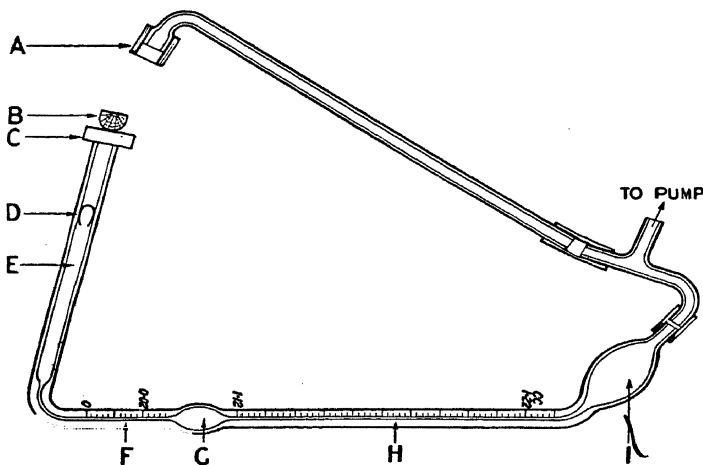


FIG. 22 (II)

of the lever, B is lifted up and the glass plate can be removed. On releasing the lever B approaches E without touching it, and as the lever is mounted on a suitably pivoted platform, B can be turned aside from over E. Enough mercury to fill E and part of F is put in ; the volumeter tilted until all the mercury flows from E into F, G, H, and I ; the rubber tube A slipped over the end of E and both limbs evacuated simultaneously. While still exhausted, the tube is tilted back again until the mercury nearly reaches the top of E and entirely covers the steel wire spring D, which is held by friction against the walls of E. Air is then admitted, the rubber tube removed, and the glass plate replaced and clamped in position again. The tube is further tilted until mercury fills E completely, the remaining air escaping between the glass plate and the ground end of the tube E, while the mercury is arrested. The position of the mercury surface is read on the graduated scale F. The tube is then tilted back until the mercury vacates E, C and D

<sup>1</sup> *J. Inst. Physics*, 1929, 6, 261.

are removed and the object, the volume of which is to be measured, inserted in E. The steel spring is put over it to prevent it rising through buoyancy. Evacuation and tilting are performed as before, and a reading on the scale H obtained. The difference between the two readings is the volume of the object. It is important that both the object and the spring are entirely covered by mercury before admitting air to the exhausted tube.

Tilting should be slow and controllable with nicety; a mechanical device is almost essential. An irreversible worm and wheel have been used for larger sizes, a frictional reducing gear with locking device for smaller ones.

In the apparatus shown in the figure the length of E is 110 mm., internal diameter 8 mm., length of the capillary limb 200 mm., capacity of the bulb G about 1.1 ml., but these dimensions can be altered to suit other types of solids.

**Liquids.** The determination of the exact volume of a liquid is usually accomplished, if its density be known, by a weighing method (see chapter on Density), or by a direct comparison of the volume in question with that of a standard graduated vessel in which it is placed. It is necessary to calibrate this vessel accurately, whether it be flask, pipette, or burette, and this subject, together with other points which arise in the volume of liquids, is considered in detail below. In accurate work all measuring vessels must be standardized carefully either by the maker or user, or by an institution such as the National Physical Laboratory. For the very highest precision standardization *ab initio* should be undertaken and the standardized instruments, especially if in constant use, be checked at intervals.

Lunge and Rey's glass tap pipette (Fig. 23 (II)) is a convenient apparatus for the measurement of small volumes of liquid, especially with fuming substances. The tap should be tight without greasing. A partial vacuum is made in the bulb and the lower tap is then opened with the point under the surface of liquid to be tested (after removal of cover). Liquid is then sucked up into bulb. The lower tap is again closed. The apparatus is weighed before and after these operations and the difference in weight is equal to the weight of liquid introduced.



FIG. 23 (II)

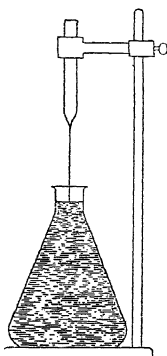


FIG. 24 (II)

In determining the volume of very viscous liquids it is difficult on account of the physical nature of the material to read off its volume with any degree of accuracy in a graduated cylinder. The measurement of volumes may be made in the following way.<sup>1</sup> A capillary tube is clamped in a fixed vertical position so that it dips into the neck of the dry conical flask which is always placed in a definite position (Fig. 24 (II)). Water is accurately measured in from a burette until the surface of the water in the flask reaches the capillary tube. This point is sharply indicated by a rise of water in the capillary tube, and the volume of water run in is taken as the volume of

the flask. The same procedure is carried out on the flask containing the

<sup>1</sup> Donnelly, Foott and Reilly, *Sci. Proc. Roy. Dubl. Soc.*, 1929, XLVIII, 20, 101.  
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tar or other viscous liquid, the difference in the two volumes gives the volume of the tar.

**Gases.** The measurement of gas volumes is considered in a later chapter. It needs special consideration since the volume of a gas cannot be determined apart from its pressure.

### MEASUREMENT OF THE VOLUMES OF LIQUIDS

Owing to the property possessed by liquids of adjusting themselves to the shape of the vessel containing them and to the fact that their volume is not greatly altered by any external pressure to which they may be subjected, the determination of a liquid volume is, in the laboratory, a simpler matter than the determination of a gaseous or solid volume, and, as indicated, is often employed to fix either of the other two.

**Vessels Employed.** The three types of measuring vessel most generally applied to the accurate measurement of liquid volumes are: (a) the flask, (b) the burette, and (c) the pipette; preferably they are constructed of thin non-reactive glass, well annealed and free from striae. Vessels such as flasks and the like provided with a flat base should stand firmly upon it without rocking. Outlet or inlet tubes, stoppers, taps, &c., should be water-tight and should not project into the measuring space.

**Cleansing of Vessels.** The first essential in the standardization of glassware is to have the vessel to be examined thoroughly clean. Slight traces of grease are particularly to be avoided. They are often difficult to remove, and when present in vessels undergoing standardization may lead to serious errors. The following process is recommended. The flask or other vessel is first thoroughly rinsed with water and mechanically cleansed of as much impurity as possible in the ordinary way. It is then filled with a cold concentrated solution of potassium dichromate in an equal volume of concentrated sulphuric acid, and thus filled, is allowed to stand for six hours or more. The solution is then poured off and the vessel drained and washed with distilled water. On no account must any standard vessel be heated, as this may alter the volume to some extent. If grease is still present, as indicated by the liquid clinging to the inner surface of the vessel in patches, the process is repeated, if necessary, for a longer period, or the vessel is filled with fuming nitric acid and treated as above. After the thorough washing with distilled water the vessel is dried by rinsing with pure alcohol and then with pure ether, being afterwards placed in a current of pure dry air, filtered through cotton-wool. Pure acetone may also be employed to remove water. With the introduction of solvents there is some risk of a trace of grease being deposited. If the vessel is dried in a current of purified warm air without solvents this risk does not arise.

### STANDARDIZATION OF THE FLASK

The standard flask is most usually employed to obtain a known volume of a liquid. Various forms of the flask are shown in Fig. 25 (II). The usual form of flask consists of a body forming the main portion of the volume and a long narrow neck on which a mark indicates the required capacity at a

given temperature ; what the capacity and temperature are is usually etched on the flask. The body is shaped so that the flask stands firmly while the neck is made as narrow as is consistent with convenience, in order that any unavoidable divergence of the level of the liquid from the mark may lead to an error smaller than other experimental errors, due to the influence of temperature, pressure and the like. These errors are usually about 0.05 per cent, varying from 0.08 per cent with a 10 ml. flask to 0.02 per cent for litre

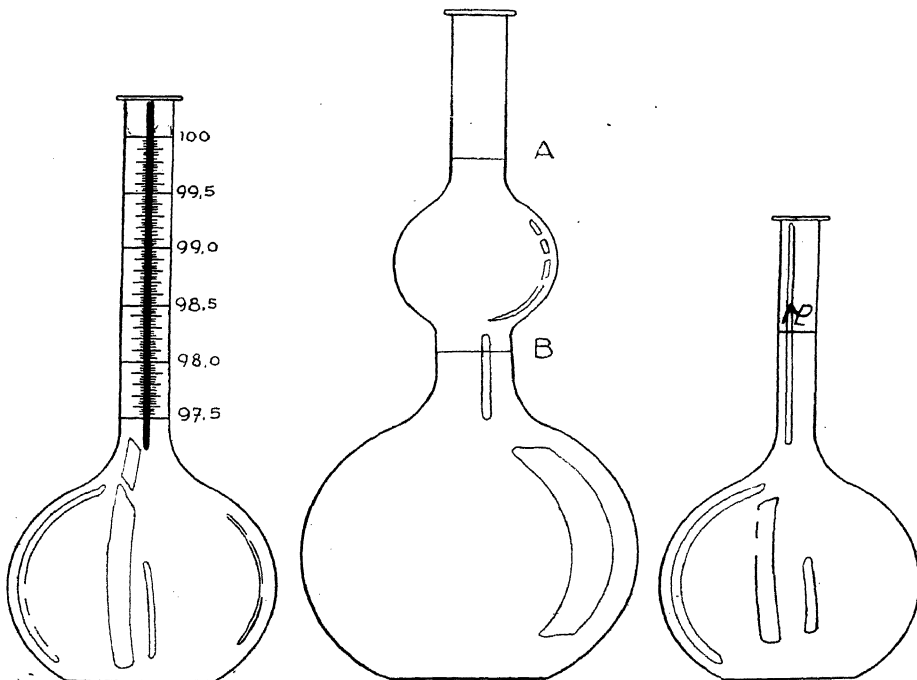


FIG. 25 (II)

and larger flasks. So if a flask be marked to contain a litre at a given temperature, and if it be assumed that the liquid can be made to coincide with the fixed mark to within 1 mm., then the neck must have an inner diameter not greater than approximately 1.3 cm. With smaller flasks the narrowness of the neck necessary makes it difficult to mix the contents by shaking. The difficulty is overcome in the Regnault flask by providing a neck widened at the top as in the figure.

**Method of Standardization.** The method used in standardizing a flask and most measuring vessels graduated to contain a given volume involves the weighing of the vessel filled with a liquid of known density, such as water or mercury, and also weighing the same vessel empty. Corrections must be applied for the buoyancy of air, for temperature, and also for the meniscus effect of water or mercury (see later). Mercury gives a greater

weight than water for a given volume, and thus yields more accurate results, especially with small volumes; with larger volumes the internal pressure it exerts is too great, tending to distort or to break a vessel; also the differences in weight involved are too large to be convenient; water is consequently here employed. The latter liquid is more readily obtained pure; on the other hand, the fact that mercury does not wet many surfaces, for example, glass which has not been freed from adsorbed gas by heating in a vacuum, enables volumes to be determined accurately by filling them with mercury and pouring into a graduated vessel or into a vessel which can readily be weighed. Care must be exercised if the volume under investigation be irregular in shape, as the high surface tension of mercury may prevent its filling sharp angles.

The details of the method of standardization are as follows: The clean dry flask is counterpoised on an accurate balance and is then filled with distilled air-free water or pure mercury at room temperature to the mark on the neck, so that with water the bottom and with mercury the top of the meniscus coincides with the mark. This coincidence is obtained with mercury by filling almost to the mark and then adding mercury drop by drop, since mercury standardizations are best carried out using a rising meniscus. With water the opposite holds. The vessel is carefully filled to a few millimetres above the mark, care being taken to avoid wetting the neck above this level. The surface is then adjusted to the mark by removing small quantities of water with a fine capillary tube. In making these adjustments care must be taken to avoid errors due to parallax.

The apparent weight  $P$  of the water contained in the flask is then determined and the temperature  $t^\circ$  is noted. Table A<sup>1</sup> gives the value  $R$ , which, when multiplied by  $P$ , yields the exact volume of the liquid contained by the vessel filled to the mark, as described, at  $t^\circ$ , compensation being effected for the change in density of the standard liquid with temperature and also for the buoyancy effect of the air. The coefficient  $R^1$  gives the volume of the liquid at temperatures  $t' = 10^\circ, 18^\circ$  and  $25^\circ$  respectively, from observations taken as before at  $t^\circ$ . It is assumed that brass weights are employed. The exact volume of the vessel to the mark may be obtained by applying the meniscus corrections (see later). The apparent weight, i.e. the weight in air of 1 ml. of water at various temperatures, is proximally obtained from the above table by subtracting from unity the figures in the value of  $R$  for water to the right of the decimal point. The apparent weight of a millilitre of mercury can also be deduced from the table, but not by such a direct method.

For water saturated with air the density between  $0^\circ$  and  $13^\circ$  is diminished by 3 units in the 6th decimal place; between  $14^\circ$  and  $17^\circ$ , by 2 units; between  $18^\circ$  and  $19^\circ$ , by 1 unit; above  $20^\circ$  the differences are negligible. It will thus be seen that, except in very accurate work, it is unnecessary to take any special precautions to ensure that the water employed to standardize a vessel is free from dissolved air.

**Derivation of Table.** If a glass vessel at  $t^\circ$  weighed with brass weights, in air of specific gravity 0.0012, be found to contain  $P$  grams of water or mercury, then its volume in millilitres at  $t^\circ$  is

$$V = PR = Pp/d,$$

<sup>1</sup> Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 1923, Vol. I, 78.

where  $p$  is the factor for reducing the weight in air to vacuum and  $d$  is the specific gravity of water or mercury at  $t^\circ$ .

At another temperature  $t'^\circ$

$$V = PR' = P(1 + (t' - t)\gamma)p/d$$

where  $\gamma = 0.000025$ , the cubical coefficient of expansion of glass.

TABLE A

WATER					MERCURY			
$^\circ\text{C.}$	R	R <sup>1</sup> for $t = 10^\circ$	R <sup>1</sup> for $t = 18^\circ$	R <sup>1</sup> for $t = 25^\circ$	R	R <sup>1</sup> for $t = 10^\circ$	R <sup>1</sup> for $t = 18^\circ$	R <sup>1</sup> for $t = 25^\circ$
	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .	cm <sup>3</sup> .
0	1.001193	1.001443	1.001643	1.001818	0.0735501	0.0735685	0.0735832	0.0735960
1	1133	1359	1559	1734	5636	5802	5949	6077
2	1092	1292	1492	1668	5771	5918	6066	6194
3	1068	1243	1443	1618	5907	6035	6183	6311
4	1060	1210	1410	1586	6037	6147	6294	6423
5	1068	1193	1394	1569	6172	6264	6411	6540
6	1092	1192	1392	1568	6308	6381	6529	6657
7	1131	1206	1406	1581	6492	6547	6695	6824
8	1184	1234	1435	1610	6628	6665	6812	6941
9	1252	1277	1477	1652	6763	6782	6929	7058
10	1333	1333	1534	1709	6894	6894	7042	7171
11	1428	1403	1603	1779	6975	6975	7104	7233
12	1536	1486	1686	1862	7111	7074	7222	7351
13	1657	1582	1782	1957	7241	7186	7333	7463
14	1790	1690	1890	2066	7377	7304	7451	7581
15	1935	1810	2010	2186	7513	7421	7569	7698
16	2092	1942	2143	2318	7644	7533	7681	7810
17	2261	2086	2286	2462	7780	7651	7798	7927
18	2441	2241	2441	2617	7911	7763	7911	8039
19	2633	2407	2608	2783	8047	7881	8028	8157
20	2835	2584	2785	2960	8183	7998	8146	8275
21	3047	2772	2972	3148	8314	8111	8258	8398
22	3271	2970	3170	3346	8450	8229	8376	8505
23	3504	3178	3379	3554	8581	8341	8489	8618
24	3748	3396	3597	3773	8717	8459	8607	8736
25	4001	3624	3825	4001	8848	8571	8719	8848
26	4264	3862	4063	4239	8985	8689	8837	8966
27	4537	4110	4310	4486	9116	8802	8950	9079
28	4819	4367	4567	4743	9253	8920	9068	9197
29	5110	4633	4833	5009	9384	9033	9181	9310
30	5410	4908	5109	5284	9520	9151	9299	9428

For example, the density of mercury at  $0^\circ$  is 13.596, and its specific volume, the volume of 1 gram, is 0.007355 ml. Its cubical expansion coefficient is 0.0001817. If, therefore,  $P$  is the weight in air using brass weights of that amount of mercury which at  $t^\circ$  fills a space  $V$ , then

$$\begin{aligned}
 V &= \frac{Pp}{13.596(1 - 0.0001817t)} \text{ ml.} \\
 &= Pp(0.007355(1 + 0.000182t)) \text{ ml.}
 \end{aligned}$$

In all these determinations the volume of the air displaced by the glass of the flask need not be considered, as the flask is counterpoised both full and empty and the effect is eliminated in the subtraction to obtain the apparent weight of the liquid. The factor for correcting for the buoyancy of air must be determined either accurately or approximately according to the accuracy of the main determination. The value taken in the table is that given in the next section, and the table thus constructed will suffice for most purposes. For extremely accurate work all the constants involved, e.g. the coefficient of expansion of the glass of the vessel, must be determined separately by measuring the volume at several temperatures before interpolation for other temperatures can be attempted.

**Marking of Flask.** If the flask is incorrectly marked another mark is made and the volume to this mark determined. The position on the neck for the volume required can then be calculated readily, assuming that the neck is perfectly cylindrical. The flask is then filled to this point with water and liquid added or removed by means of a pipette until the correct apparent weight for the volume desired is obtained. This weight is previously calculated. Any water which may get on the neck above the mark is removed by means of filter paper. A mark is then etched on the neck at the point indicated, which can be marked provisionally by a strip of gummed paper. The method of graduating an unmarked flask will be obvious.

To etch a mark on the flask at the indicated spot the whole is covered with wax, and where the ring is to be marked the wax is removed by means of a stylus. The flask is then exposed to the action of hydrogen fluoride, when a dull mark is obtained on the exposed portion and the wax removed by a solvent. If aqueous hydrogen fluoride is employed, a transparent mark is produced.

Great care must be taken that the mark is accurately horizontal when the vessel stands on a horizontal table, so that the meniscus surface can be brought truly into line with the mark. If desired, the one flask may be marked to contain a given volume at a number of neighbouring temperatures, but for accurate work this is not recommended.

The flask, graduated as above, will contain a given volume of water, but will not deliver it owing to the moisture which adheres to the interior wall. With mercury, which does not wet glass unless the surface by heating or otherwise is completely freed from adhering air, this difficulty does not arise.

**Delivery Flasks.** Flasks graduated to deliver a given volume of liquid are not often employed. To standardize such a flask it is filled to a mark and emptied into a glass by gradually inclining it; when the continuous stream of liquid has ceased it should be nearly vertical. In this position it is allowed to drain for half a minute and the lip is then stroked against the glass, which is weighed empty and with the liquid as above. The method of calculating the volume delivered will be obvious from what has been said. If necessary a flask, by means of determinations to two marks on the neck, can be graduated on the lines indicated above accurately to deliver a given volume.

The graduation of vessels to deliver a given quantity of liquid will be discussed in more detail under 'Pipettes'.

**Meniscus Effects.** The meniscus of mercury is convex, that of water is concave, so that if the usual method of reading to the top of the meniscus

with mercury and to the bottom with water is adopted in determining the content of a flask with each of these liquids a difference will be introduced, and the volume found with the former will be slightly smaller. Generally, with any two liquids the differences in the volumes found for a flask to a given mark will be the algebraic difference between the volumes of the meniscus in the two cases. Hence, a flask which has been graduated by means of mercury will not be marked correctly for use with water. The error also operates, but in the opposite direction, if eudiometer tubes or the like are standardized by filling to a mark with a standard liquid and weighing (see Measurement of Gases).

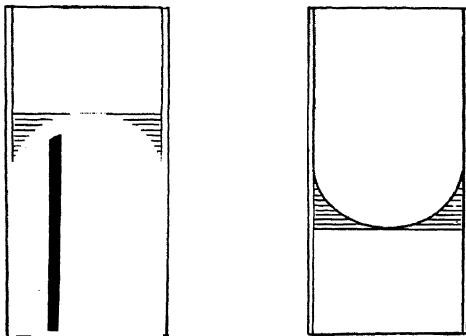


FIG. 26 (II)

**Meniscus Corrections.** The following table (B) gives approximately the volume between the meniscus and the glass wall of the vessel for both water and mercury. In Fig. 26 (II) this volume is indicated by shading.

TABLE B

Diameter of neck of flask	Volume of shaded portion	
	(Water)	(Mercury)
(cm.)	(ml.)	(ml.)
0.6	0.022	0.012
1.2	0.102	0.066
1.8	0.249	0.127

To illustrate the application of these corrections, assume that a flask to a given mark contains 100.267 ml., the graduation being accomplished by means of mercury. If the neck of the flask has a diameter of, say, 8 mm., then the actual volume to the mark measured with a hypothetical liquid which does not give a meniscus effect is  $100.267 + 0.041$  ml., and the volume of water contained by the flask filled to the mark is  $100.267 + 0.041 + 0.029$  ml. The total correction, it will be observed, is greater than the error allowed. For the application of this correction in graduating eudiometer tubes, see chapter on the Measurement of Gases.

The above table can only be used with water and mercury, but more general tables can be constructed for the difference in millilitres between the volume of liquid contained in a flask when it is filled with water and when it is filled with some other liquid. The necessary corrections can be obtained from tables of the volume of the meniscus of, say, mercury in tubes of a given diameter. In very accurate work allowance is made for different heights of

meniscus in a tube of given diameter, owing to different temperatures, pressures and the like. Such tables are given in Landolt-Börnstein.

These meniscus corrections do not often arise with vessels graduated for delivery, for these must be standardized separately for each liquid which wets the walls of the vessel, owing to the varying amounts of liquid which adhere thereto. With liquids which do not wet the walls, the volume contained is the same as that delivered, and a meniscus correction can be employed to pass from one liquid to another.

**Standardized Flasks.** A flask which has the Class A certificate of the National Physical Laboratory must be correct to within about 0.05 per cent while the inner diameter of the neck must lie within a limit a little greater than that calculated, as already described. This applies both to content and delivery flasks.

A flask may be graduated if desired for both content and delivery, provided that the two marks are not less than 1 mm. apart. Flasks so graduated bear the letter *d* above the upper mark and the letter *c* below the lower mark. The temperature of standardization, the rated capacity and the letters NP are etched on all these flasks.

### THE BURETTE

The burette is employed to deliver desired quantities of liquid ranging in volume between 0.1 ml. and 100 ml. It consists of a cylindrical tube graduated for the larger volumes in tenths of a millilitre and holding a total volume of liquid of the order of 25 or 50 ml. At the bottom it is fitted with a glass tap (Fig. 27 (II)), or, for use with liquids such as sodium hydroxide solution, which cause the glass tap to stick, with a rubber tube connected to a glass outlet tube and closed with a pinch clip. The latter cannot be employed with certain liquids, such as permanganate, and is unsuitable for accurate work. It is of advantage to have the glass tap sloped to reduce the risk of its falling out. An arrangement sometimes employed with corrosive liquids consists of a small glass ball placed between two glass tubes which are connected by a rubber tube. In this case no tap is required, if the glass bead and rubber connections are of proper size. A slight pressure on the rubber allows a slow flow of liquid.

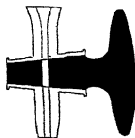


FIG. 27 (II)

As the diameter of a burette is usually greater than that of a pipette, *q.v.*, the accuracy obtainable is less, and the readings can seldom be depended on to within less than 0.05 ml., which is usually the quantity of water delivered in one drop from the tap. Burettes holding 10 ml. with a narrow bore and graduated in 0.01 ml. can, however, be obtained. These are fitted with special taps to produce the necessary fine drops. Ordinarily, the diameter of a burette should be as small as possible consistent with convenience in length; a 30 ml. burette, for example, has usually a diameter of 8–9 mm. The jet of a burette should be made with a gradual taper, a sharp constriction being avoided. The end of the jet must be ground off true and the ground surface made smooth. The graduation marks should be clean and fine and should lie parallel to

each other and in planes perpendicular to the axis of the tube. The distance between two adjacent marks must not be less than 1 mm.

**Standardization.** Burettes are standardized by a general method proposed by Ostwald, which is on the same lines as that used for flasks. It involves the use of a small pipette of about 2 ml. capacity fitted with a tap (Fig. 28 (II) ), and which has two marks at the positions indicated. It is fused to the burette as shown, and is first standardized before being applied to the standardization of the burette. For this purpose the latter must be cleansed thoroughly (see earlier). It is rinsed out by filling with the liquids described, inverting and opening the tap. This produces a good flush through the burette and facilitates the operation.

The clean burette is clamped vertically, connected to the pipette, and filled with distilled water; the latter is also filled to the mark X through tap on left. The pipette is run out to the Mark Y, being allowed to drain for one minute before the level at Y is adjusted. The water collected is weighed accurately. From a number of determinations the weight of water at a definite temperature which fills the pipette between the marks is calculated, and hence the volume of the pipette fixed, allowance being made for temperature, buoyancy of air, &c. (see Table A). These separate determinations must agree closely, otherwise it points to the instrument not being clean. In filling the pipette from the burette it is of importance that the rate of outflow should be sufficiently slow to render negligible errors due to drainage from the walls of the burette. Further, the time occupied in emptying any interval on the burette during calibration must be approximately equal to the time required to empty the same interval on the finished burette, when the stopcock is fully open, so that the quantity of liquid left adhering to the sides remains apparently constant. With burettes from a good maker the rate of outflow will not usually be too rapid; for 30 ml. it should not be less than about 60 seconds. When great accuracy is required the time of outflow of a 50 ml. burette should be of the order of 180 seconds; too long a time is, on the other hand, also to be avoided. In order that the approximate same time of outflow may be obtained during direct discharge as when the liquid is being run into the standardization pipette, Stott fixes to the top of the burette a piece of thermometer tubing which is chosen so that the air flows into the burette at the required rate, this ensuring that the water also flows out as required. In running the water into the pipette it is

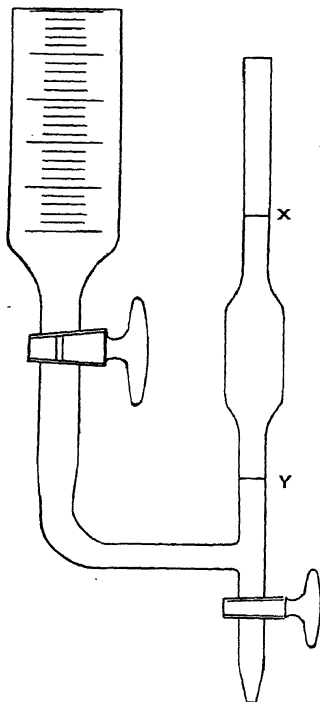


FIG. 28 (II)



essential that the tap should be opened fully each time and closed just before the water reaches the required mark. After allowing 1 minute for the burette to drain, the fine adjustment is made.

The volume of the pipette is now applied to determine the volume of the burette. The latter is filled with water accurately to the zero mark and the pipette to the mark X; the last is then run out to the mark Y, being allowed to drain for the same time as before. The burette is then read to ensure that the level of the liquid still stands at the zero mark; if it does the tap is opened and water allowed to flow into the pipette until it reaches the Mark X. The pipette is emptied to the mark Y, using the same precautions as before, while the burette is also read. The filling and emptying of the pipette is continued until the burette is run down almost to its lowest reading.

**Parallax.** It may here be emphasized that in reading and adjusting the burette and adjusting the pipette, the lowest part of the concave water surface should always be read. The necessity

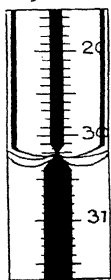


FIG. 29 (II)

for a meniscus correction is thus avoided, as the effect is the same in both observations. In carrying out the readings the eye must be placed in the same level as the water surface to avoid errors due to parallax. To facilitate this, good burettes have the graduation marks etched completely around them, so that the plane of the mark is perpendicular to the axis of the burette. The eye is then placed so that the front of the etching conceals the back portion: or a vertical mirror may be suspended behind the burette and parallax avoided in the usual way. With non-transparent liquids the margin of the meniscus is employed to fix the proper level for the eye, but the readings can never be accomplished with the same accuracy as with transparent liquids.

Apart from avoiding parallax the exact position of the meniscus is sometimes difficult to fix. The placing of a white tile behind the burette aids in giving the water meniscus a sharper appearance, especially if a piece of black glazed paper be wrapped round the burette so that the top edge of the paper is not more than 1 mm. below the bottom of the meniscus. A number of other devices are also in use; some burettes (Schellbach burettes) have, for example, at the back a piece of white glass with a blue line running down the centre; at the meniscus it presents the appearance shown in Fig. 29 (II), so that reading is greatly facilitated. These and other devices, such as the Erdmann float (Fig. 30 (II)), are convenient for routine work, but are not recommended where the highest accuracy is required.

**Mounting Burette.** Particular care must be taken in using a burette to see that no air bubbles are trapped between the tap and the lowest point of the jet. A little practice will enable all such bubbles to be removed by running out quickly a little of the liquid

11

12

13

|| ≡ || 15

≡ || 16

17

≡ ||| 18

19

FIG. 30 (II)

in the burette. In filling, it is always advisable to use a funnel, or better, to employ instruments splayed somewhat at the top to form a small funnel. Care must be taken that the axis of the burette is always vertical.

**Calibration.** The cycle of operations which has been described above, by which the burette is divided into a number of equal parts each of which discharges a volume of water equal to that discharged by the pipette in emptying from one mark to the other under certain fixed conditions, having been repeated three or four times, an average reading is taken for each discharge. These readings should agree in the case of one and the same discharge space on the burette to within 0.01 ml. ; if greater differences are obtained, it points to the instrument not being sufficiently clean and the operation must be repeated. It may be noted that water is here the only convenient liquid, as mercury is too heavy to be employed in a tall burette. From the readings which have been obtained, sufficient data are available to standardize the apparatus. The following example (Table C) will make clear the application of the data :

EXAMPLE (TABLE C)

Volume of pipette found = 2.87 ml. (average)		
Readings of burette (average)	Difference from pre- vious readings	Difference from 2.87
0.0	—	—
2.86	2.86	— 0.01
5.72	2.86	— 0.01
8.56	2.84	— 0.03
11.40	2.84	— 0.03
14.26	2.86	— 0.01
17.13	2.87	0
20.01	2.88	+ 0.01
22.90	2.89	+ 0.02
25.79	2.89	+ 0.02
28.67	2.88	+ 0.01
31.54	2.87	0
34.42	2.88	+ 0.01

A curve of corrections (Fig. 31 (II) ) is then drawn, the burette scale being shown along the abscissae and the corrections as ordinates. The calibration as carried out above is, strictly speaking, valid only for water and dilute aqueous solutions, owing to the varying quantities which will adhere to the sides of the burette. For other liquids a separate determination, using the specific liquid, must be employed.

If preferred, the marks on the pipette employed for the standardization may be adjusted so that the volume contained between them is an exact number, 1 or 2 ml. This process may also be applied to the standardization of a burette *ab initio*, but the necessity for this seldom arises in a physico-chemical laboratory.

**Alternative Method of Standardization.** The standardization of a

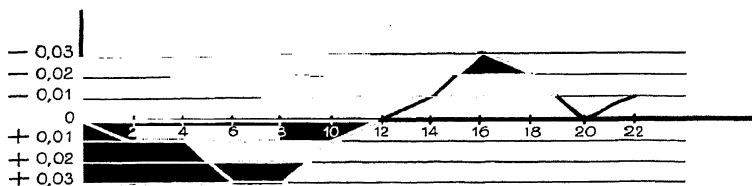


FIG. 31 (II)

burette can also be carried out by running the water directly each time with the tap fully open into a clean weighed vessel until the meniscus falls from the zero mark to the mark to be tested. The drop adhering to the tip of the burette is removed by bringing the tip in contact with the side of the receiving vessel. Precautions regarding drainage, adjustment of the meniscus, and the like are applied as described above, and from the weight of water delivered the volume is calculated. This method is somewhat more accurate than that of Ostwald, since the burette is standardized exactly under the conditions in which it is to be employed, but it is more tedious, as a much greater number of weighings are required.

**Tolerance.** In a good burette the errors between the indicated markings and those obtained by this method of standardization will not exceed some hundredths of a millilitre, provided some 60 seconds be allowed to elapse after running out a quantity of liquid before reading. The following indicates the limit of error allowed in a first-class burette:

Vessel holding up to 30 ml.	0.03 ml.
" " 30 to 50 ml.	0.04 ml.
" " 75 to 100 ml.	0.07 ml.

Burettes accurate to this degree and bearing the Class 'A' Certificate of the standardization of the National Physical Laboratory can now be purchased from all the leading manufacturers of chemical apparatus. The content, the temperature at which the instruments are to be employed, and the time of outflow, are all etched on these instruments. The last figure must be accurate to about  $\pm 8$  per cent, and should be tested at intervals. Any departure from the limits prescribed shows injury to the jet, and the burette should either be rejected or the time of outflow adjusted as described later.

**Manipulation.** Where a large number of titrations employing one liquid have to be performed, the apparatus shown in the figure is of use (Fig. 32 (II)); the burette is filled from the larger container by suction, at the rubber tube. Another apparatus to achieve the same results is shown in Fig. 33 (II), where the burette is automatically filled to the zero mark by blowing up liquid by pressure on the rubber bulb; the functioning of the automatic level adjusting apparatus will be clear from the diagram. Standard solutions and the like may be kept for long periods in such an apparatus without undergoing change through evaporation. In this connec-

tion the use of pressure for transferring the liquid to the burette is to be preferred. It is necessary, where a titration is to be carried out after a period of rest, to wash out the burette with the liquid. Alternatively, the burette may be kept always filled with the liquid and corked. Where liquids such as baryta solution are being titrated the burette and the bottle containing the bulk of the liquid must be protected by soda lime guard tubes (see Fig. 34 (II) ), arranged as shown, to economize in height and to prevent any

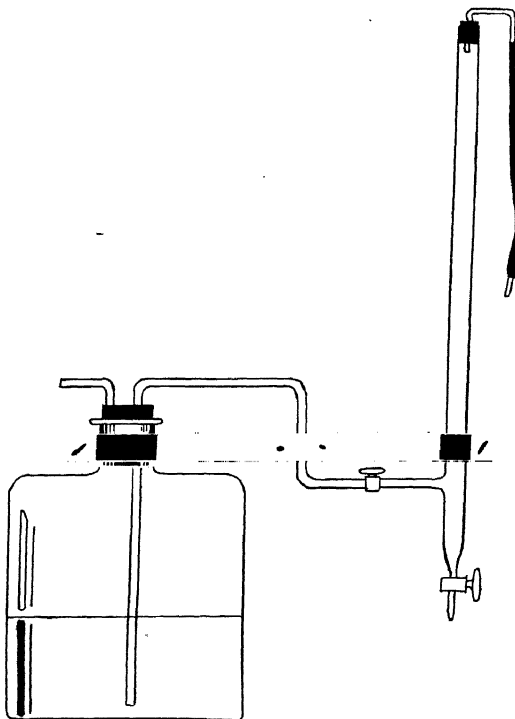


FIG. 32 (II)

of the absorbent from dropping into the burette. For the purposes of titration in which the quantity of liquid required is known approximately to fall above or below a definite amount, such as 25 ml., a burette may be employed fitted with a bulb at the top holding a definite quantity of liquid between two marks—say 25 ml. The lower portion is made to contain 25 ml., and is graduated downwards from the lower mark on the bulb in the usual way. The bulb is employed when larger quantities of liquid than 25 ml. are required. This arrangement reduces the height necessary for a 50-ml. burette (Fig. 35 (II) ).

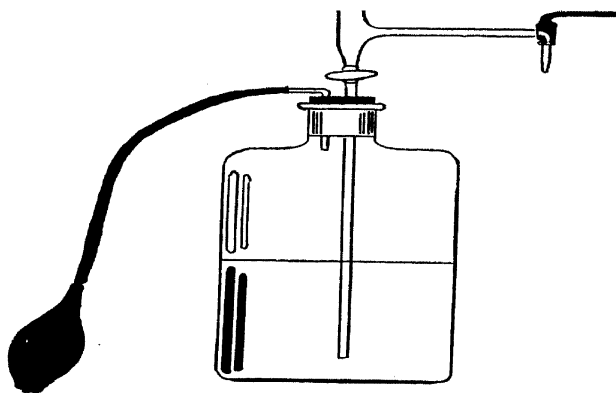
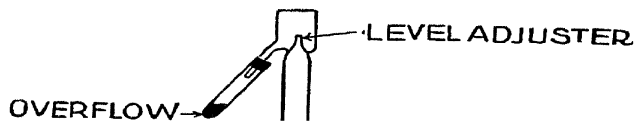


FIG. 33 (II)

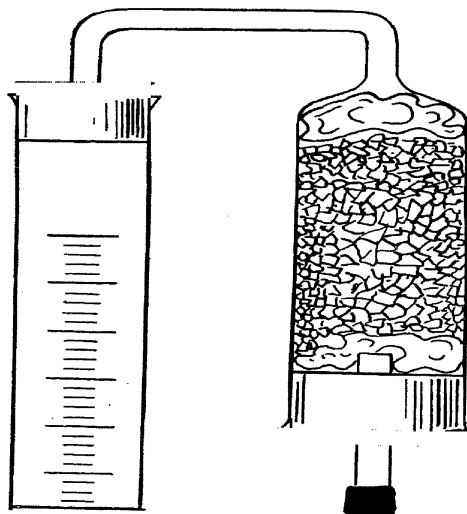


FIG. 34 (II)

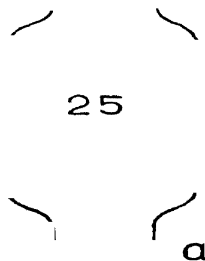


FIG. 35 (II)

## PIPETTES

**Their Use.** The pipette is mostly employed to deliver fixed quantities of liquid up to about 100 ml., and is usually of the form shown in Figs. 36 (II) or 37 (II). The length of the delivery tube below the bulb should be at least 5 cm., otherwise drainage errors which cannot be allowed for are introduced. The top of the suction tube is ground off square and the



FIG. 36 (II)



FIG. 37 (II)

ground surface is rendered smooth; the delivery tip, as with all vessels of this type, must be made with a gradual taper. Further, the expansions of the suction and delivery tube to meet the bulb must be sharp, so that liquid may not be caught at these points. The delivery tip is adjusted, if necessary, by treatment in a flame, so that the time of outflow of the pipette (e.g. until the liquid ceases to flow from it) falls within the following limits (Table D):

TABLE D

Capacity, ml. . . . .	2	5	10	50	100
Minimum delivery time, seconds . . . .	5	10	15	20	30
Maximum delivery time, seconds . . . .	10	20	30	40	60

If the period of delivery is too rapid a comparatively large and variable volume remains adhering to the sides of the pipette ; too long a period means undue absorption of the users' time with no corresponding gain in accuracy.

After the pipette has ceased to flow, the meniscus coming to rest just above the tip, it is allowed to drain for a fixed time, preferably 30 seconds. This drainage and removal of the last drop of liquid to be delivered is a matter of some importance. It is preferable to place the tip against the side of the vessel and hold it there during the draining period. The last drop after out-flow has ceased is sometimes blown out, or the top of the pipette is closed by the finger and the bulb warmed by the hand. Neither of the latter methods is recommended, but it should be emphasized that whatever method is adopted in the standardization should be continued in the subsequent use of the pipette in order to obtain concordant results.

The width of the stem of a pipette is a matter of importance, for it should be as small as is consistent with the strength necessary to render the pipette serviceable, so that errors due to the bottom of the meniscus not being quite in line with the mark may be reduced to the same order as the other errors in the use of the instrument ; these other errors are usually found to be of the order of 0.05 per cent of the total volume of the pipette. If we assume that the level of the liquid can be determined to within 1 mm. it at once follows that the diameter of the stem of a 1-ml. pipette should be 1 mm. ; of a 10-ml. pipette 3 mm., and so on. It is difficult to obtain great accuracy with 1 and 2 ml. pipettes if they have the usual shape of these instruments. Accuracy to 0.05 per cent can, however, be obtained by the employment of pipettes with the shapes shown. The jet of the instrument is drawn out of the tube which forms the bulb, while the neck, which may be 1-2 mm. wide, is sealed on. The tip is drawn out so that the time of discharge is about 1 minute.

**Standardization.** The method of standardizing a pipette will be clear from what has been given on the standardization of burettes. The clean pipette is filled to the mark, temporary or permanent, with pure water ; this is best accomplished by suction with an air bulb, as the process is then more readily controlled than if the mouth be employed. With small pipettes of, say, a capacity of about 1 ml., mercury may be employed. The clean pipette full of liquid is discharged into a tared receptacle, and the weight of the liquid it contains determined with the usual precautions. The operation is several times repeated and the mean result taken. It is necessary that there should be substantial agreement between the results used to obtain a mean ; if not, the instrument is not quite free from dirt, probably grease, and the whole

operation must be repeated *ab initio*. As emphasized before, in discharging the pipette it is essential that the pipette be allowed to drain for a fixed time and then touched once against the side of the vessel, or it may be blown out at the end; whichever practice is adopted must be followed consistently. The mean of the weights obtained gives the quantity of standard liquid discharged by the pipette under the conditions of the standardization; the discharge volume of the pipette can then be obtained immediately, as already described. The volume can also be calculated for another temperature, but not so accurately as with a flask, if water be the liquid used, as the amount of liquid adhering to the walls of the vessel will vary with temperature. The same considerations apply to the burette, and to all vessels calibrated for delivery. The pipettes which are graduated like burettes are standardized in a similar manner. If desired, a mark corresponding to a desired volume can be etched on a pipette, following the lines previously described.

**Temperature Effects.** Regarding the effect of temperature on the capacity of pipettes and of all standard glassware, the expansion effect of the glass may, in most cases, be neglected, a change in temperature of  $1^{\circ}$  only altering the volume by a quantity of the order of 1 part in 40,000. If the volumes delivered are being employed to measure liquid masses it is, of course, essential to correct for the change in density of the liquid with temperature. The coefficient of expansion of water is about 1 part in 5,000 at ordinary temperatures; that of the common organic liquids is much higher, being of the order of 1.5 parts for 1,000.

It is advantageous to keep pipettes immersed in a solution of potassium bichromate and sulphuric acid. They are well rinsed with distilled water before use.

**Automatic Pipettes.** Pipettes which automatically deliver a given quantity of liquid are shown in Figs. 38 (II) and 39 (II), and are often convenient. The type in which the overflow can be run back into the pipette after use by rotating the bored stopper has certain advantages.

**Standardization of 'Content' Pipette.** In some physico-chemical operations it is necessary to draw an exact volume of liquid from a larger volume, as, for example, if it were required to take out an exact volume of a solution of known volume in order to examine its strength. To calibrate a pipette for this purpose a stoppered flask containing water is weighed with the usual precautions and then, by means of the pipette, water to fill it to the mark is withdrawn and the flask reweighed. The difference in the weights gives the volume of liquid removed by the pipette, allowance being made for the density of water at the temperature of the standardization. By employing two marks, as already described, and calibrating the stem between them, a mark corresponding to a definite volume can be obtained and etched on the neck. In accurate work the conditions under which the pipette is employed must be standardized; for example, the pipette must each time be immersed the same distance into the liquid in order that the same quantity of liquid may each time remain adhering to the outside of the discharge tube of the pipette.

**Tolerance.** In a good pipette the difference between the rated capacity for content or deliverance with both ordinary and automatic pipettes should not exceed 0.006 ml. with 1-ml. pipettes and 0.05 ml. with 100-ml. pipettes.



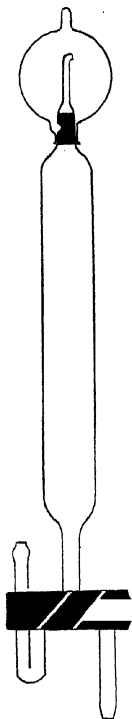


FIG. 38 (II)

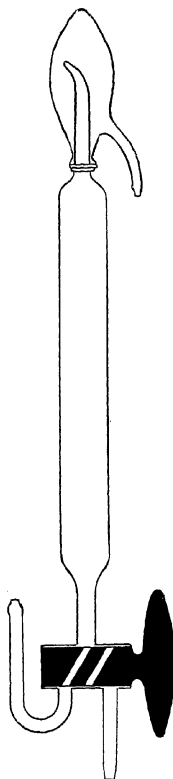


FIG. 39 (II)

These are the requirements for the Class A Certificate of the National Physical Laboratory. On such pipettes the time of outflow, which must be accurate to about  $\pm 7$  per cent, the time for which drainage is to be permitted, the temperature of standardization, and the distance in millimetres from the tip of the jet to the upper mark, are etched. The last figure enables any wear at the jet, with consequent alteration in the capacity of the pipette, to be detected.

### MEASURING CYLINDERS

**Cylindrical** measuring vessels, although in common use for rapid approximate estimation of large liquid volumes, cannot be employed for accurate work. They may be standardized both for content and delivery by the usual methods of weighing the water which they contain.

## STANDARDIZATION OF GLASS TUBES

**Calibration of a Glass Capillary Tube.** This is one of the not infrequent minor operations which must be undertaken by the physical chemist. A piece of rubber tubing is fitted over one end of the tube under investigation, which must first be cleaned out thoroughly in the usual way. By manipulation of the rubber tubing a thread of mercury is drawn into the tube by the free end and moved to various points of the tube. Its length at a number of regular intervals is measured by means of a travelling microscope and the tube thus divided into a number of portions of equal volume. The volume of the thread is determined by forcing it out on to a tared watch-glass and weighing it; in calculating the volume the usual corrections must be applied for temperature, &c. The cross-section of the capillary at any point can also readily be determined from these measurements.

**Calibration of a Glass Tube Closed at one End.** To calibrate a fairly wide tube closed at one end, a small cylindrical glass vessel with an accurately plane top edge is provided (cf. specific gravity bottle, later). On this plane edge a ground-glass plate fits. The whole is thoroughly cleaned and weighed with the ground-glass plate. It is then filled to the brim with mercury and the weight obtained with the ground-glass plate fitted on. From the mean of several readings its volume is obtained in the usual way. The contents of the vessel are then poured into the glass tube several times until the latter will not hold another pouring. The height of the mercury is each time noted and the tube is thus graduated.

The influence of the meniscus can, if necessary, either be allowed for by calculation, or the meniscus can be destroyed by pouring a dilute solution of mercuric chloride on to the top of the mercury; this flattens the meniscus (see Surface Tension). The latter method is liable to lead to errors and is not recommended. The last two examples illustrate methods of attacking problems outside the range of standardization dealt with in detail. The variety of such problems is large, and in most cases they must be taken on their merits, always applying the principles outlined. Regard must always be had to the necessity for cleanliness. If secondary standards are being obtained it is, of course, essential that the primary standards should be accurate; for instance, if accurate determination of the volume of a flask is in question it is necessary that the weights used should be standard, and so on.

## SECTION 5: MASS

**Unit of Mass.** The unit of mass was originally intended to be the mass of a cubic decimetre of pure water at its maximum density. Owing, however, to the great difficulty of obtaining an exact comparison between the mass and the volume of a substance, an arbitrary unit, known as the international prototype kilogram, was selected. It is defined as the mass of a certain cylinder of platinum-iridium which is preserved at Paris. The 0.001 part of this unit is the standard gram.

**Reduction Factor.** Conversion from kilograms to avoirdupois pounds :

1 kilogram = 2.20462234 avoirdupois pounds

1 cubic foot of water at 4° = 62.43 lb.

### MEASUREMENT OF MASS

**Weighing.** This determination is one of the most important of the measurements made in physical chemistry. Various methods are employed to accomplish it, but one exceeds in importance all the rest. This method depends on the fact that at one and the same place the mass of a body is proportional to the attraction of the earth on it, and hence to the weight of the body. So that by a comparison of the weights of two bodies a comparison of their mass is also established.

The comparison is most conveniently accomplished by suspending the body under investigation at one end of a horizontal beam, and at the other a number of bodies of known mass, such that when the beam is supported on a horizontal fulcrum at right angles to its axis it balances on the fulcrum. Applying the fundamental laws of mechanics, it follows at once that the mass of the body under investigation is equal to the sum of the known masses which balance it.

This is the principle of the balance, one of the most if not the most important of the instruments used by the physical chemist. It is also one of the most accurate, since with a good balance the error in the masses compared need not exceed  $10^{-3}$  per cent of the values of these masses.

The subject being of such importance, the operation of weighing will now be discussed in detail. Generally, the body under investigation, be it solid, liquid, or gaseous, is placed in a suitable vessel (weighing bottle, &c.), the mass of which is already known in terms of standard masses, or which has been proved to be equal in mass to a fixed body. This latter is suspended at the same end of the beam as the standard masses employed to balance the body under investigation, and its container; the sum of the masses it is necessary to employ gives the required mass. The body employed to balance the container is known as a counterpoise or tare, and is preferably a body capable of a division into portions of very small mass, such as a quantity of

dry sand ; the smaller the subdivisions of which the counterpoise material is capable the more accurately can the mass of the container be equalled. The same applies to the standard masses, the values, shape and material of which will be discussed in detail under standardization of weights.

## WEIGHING, INCLUDING THE METHOD OF WEIGHING BY OSCILLATIONS

**Determination of the Rest-point and the Sensitiveness.** Before a balance can be used for accurate work it is necessary first to construct a table showing the sensitiveness at various loads. This can be calculated using the formula given, but more accurate results are obtained by direct measurement. The balance, having been carefully cleaned and set up under expert supervision in a suitable room, is carefully levelled by means of the screws and the plumb-line provided for the purpose. The pans are then wiped with a small camel-hair brush, the case is closed and the beam is carefully released, when the pointer will swing slowly backwards and forwards over the scale ; with a little practice this can be done so as to give the pointer any desired amplitude. When the amplitude has fallen to about five scale divisions the readings of the extremities of the swing are taken for five successive swings, the observer sitting directly in front of the balance to avoid parallax in the readings. The first two or three swings are always neglected to allow the beam to settle down to a steady condition. It is best to number the scale continuously from left to right rather than to call the centre division 0 and those to the right positive and to the left negative. Suppose the middle point of the scale to be numbered 10, and that the following numbers represent the turning-points observed in the experiment :

	Left.	Right.
	9.0	
		11.0
	9.1	
		10.9
	9.2	
Mean .	9.10	10.95
Resting-point = $\frac{9.10 + 10.95}{2} = 10.03$		

The pointer may be viewed through a convex lens placed in front of the scale to magnify the divisions, but this is likely to increase the error due to parallax between the pointer and the scale. When the readings of the turning-points have been taken, the beam is arrested, care being taken that this is done at the instant the pointer is at the centre of the scale. In this way jarring the knife-edges is avoided ; their movement over the planes is also avoided, owing to the fact that while the arrestment pins move vertically the ends of the beam move in the arcs of a circle. The rider is now placed on the first division of the scale, with the effect of adding 1 milligram to one pan, and the new resting-point is found in the same way as the former one. Suppose the value 6.29 is found ; this means that the addition of 1 milligram shifts the resting-point from 10.03 to 6.29, or the sensitivity with no load is

10.03 — 6.29, i.e. 3.74. The process is then repeated with 10, 20, 30, &c., grams on each pan, and from the results obtained a curve is constructed with the sensitivity plotted against the weights.

**Weighing.** To weigh an object the method of procedure is as follows : The object is removed from the desiccator and left in the balance case for 20 minutes. The beam is then released, and the zero determined by the method of oscillations. The object is placed on the left-hand pan, and a large weight or mass is put on the right-hand pan, the weights being put as near to the centre of the pan as possible, else, on releasing the beam, the pan will be set in vibration which takes some time to die down. The handle is then turned slightly, but only just far enough to see in which direction the beam is going to move ; it is unnecessary to release the beam completely. Should the weight be too large the beam is arrested, the weight removed, and the next smaller one is tried ; if the first weight is too small this is done directly. Each weight is tried in turn until equilibrium has been obtained as near as possible. When this has been done the rider is placed at the fourth division on the scale and tried ; if it proves too much it is next tried at the second division ; or if too small at the sixth, and so on until the weight to the nearest milligram is found. The beam is then released, so that it swings with a small amplitude and the turning-points of five swings are taken, and from these the rest-point (RP) is deduced. Sufficient data have now been obtained to ascertain the weight of the object. The method of calculating the exact weight is made clear by the following example :

Turning points—

	Left.	Right.
	9.0	
		11.0
	9.1	
		10.9
	9.2	
Mean . . .	9.1	10.95
	R.P. 10.03	

With the object on the left pan and 20.577 grams on the right and the rider on the seventh scale division :

Turning points—

	Left.	Right.
	9.5	
		12.1
	9.5	
		12.0
	9.6	
Mean	9.53	12.05
	R.P. $\frac{9.53 + 12.05}{2} = 10.79$	

From the sensitivity curve, the sensitiveness for 20 grams is found to be 3.70.

The R.P. has changed from 10.03 to 10.79, i.e. 0.76 divisions.  
A change of 3.70 is the effect of 0.001 gram.

$$\begin{array}{rcl}
 1.00 & \frac{0.001}{3.70} & '' \\
 0.76 & \frac{0.001 \times 0.76}{3.70} & \text{gram} = 0.0002 \text{ gram.}
 \end{array}$$

Since the resting-point obtained with the weights on the pan was greater than the zero, the weights were insufficient, and the 0.0002 gram must be added to the 20.577 grams; the total weight is thus 20.5772 grams. If the weight is large it is worth while taking the zero after the weighing as well as before and using the mean of the two values.

**Precautions in Weighing.** A centigrade thermometer reading to 0.1° should be kept in the balance case and its reading taken each time a weighing is made; the barometric height should also be recorded. These are required for the vacuum corrections.

Objects must never be weighed until they are at the same temperature as the balance case. A polished platinum crucible, for example, after heating, should be allowed to remain for twenty minutes in the desiccator and ten minutes in the balance case, whereas a large porcelain crucible, e.g. a Gooch crucible, really requires an hour to reach equilibrium, but this may be shortened to half an hour, provided the same time is allowed to elapse throughout any series of experiments.

Large flasks after heating or rubbing require six hours to attain this equilibrium, and although polished platinum reaches a steady state very quickly, roughened platinum surfaces may take longer than porcelain or glass. However, except in work of the highest accuracy this long time is not allowed, a period of about 20 minutes sufficing, in which time the greater part of the change will have occurred, and if exactly the same time period is allowed each time the resulting error will be small.

The use of a small quantity of radioactive substance such as uranium oxide in the case to dispel electric charges produced on glass or quartz apparatus in the process of wiping preparatory to weighing has been recommended. Glass or quartz weights, it is claimed, become electrified by friction with the velvet lining of the weight box, and such charged bodies would be attracted by near objects, but it is unlikely that this factor will cause even a small error in weighing.

It is useless to weigh with great accuracy large pieces of rubber, coal, glass or platinum, which, owing to adsorption or loss of moisture, often change in weight by some milligrams in successive weighings. This variation is especially noticed in the weighing of finely divided coal, and several authorities state that in such weighings no desiccating agent should be used in the balance case.

Objects should never be weighed beyond the accuracy of the whole determination. For instance, in weighing out materials for standard solutions accuracy to the third decimal place will often be sufficient, owing to the limited accuracy of the volumetric determinations.

In weighing an anhydrous powder, the operations should be carried out as quickly as possible to prevent adsorption of moisture. It may facilitate

matters to some extent if the large weights are placed on the pan before the vessel containing the powder is added ; e.g. if a crucible weighing 25 grams is being used and the weight of the powder is estimated to be 2 grams, 27 grams may be placed on the pan in readiness. If the object is of such a size that it will conveniently go into a stoppered containing vessel, this can be used with advantage, the vessel being placed in the desiccator with the crucible, and the latter when cooled being placed in the stoppered vessel and transferred to the balance, left the usual 20 minutes to approach equilibrium, and then weighed. The same procedure of course must be adopted in obtaining the weight of the empty boat or crucible.

Powders should be weighed in glass-stoppered weighing bottles and then transferred to the reaction vessel, the bottle and the remaining powder being weighed afterwards, the weight of the powder being obtained by difference. Salts containing water of crystallization should not be placed in the desiccator previous to weighing, but should be weighed air-dry. Liquids will evaporate in the balance case, and are therefore weighed in stoppered vessels or in one of the numerous weighing pipettes made for the purpose.

**Borda's Method of Weighing.** When large glass or porcelain vessels containing reagents have to be weighed before and after a reaction, Borda's method of weighing by tares is useful, because in these cases the vacuum corrections would otherwise be large, and owing to their uncertainty might cause large errors. The zero is first determined as usual, and the object to be weighed is placed on the left pan ; the tare should be of the same material and of nearly the same weight, volume, and surface area as the object ; the tare is placed on the right pan, and small weights are added to one pan to get equilibrium, and the R.P. is calculated. From this we get that the object is equal to the tare, plus small weight  $w$ . After the reaction the object is again weighed against the same tare, and the alteration in weight is thus determined. The tare should receive exactly the same treatment as the object weighed ; i.e. if the latter is heated to redness and then cooled in the desiccator for half an hour, the tare must similarly be heated and cooled. To eliminate all necessity for vacuum corrections the alteration in weight involved must be small compared with the other weights.

**Method of Double Weighing.** In most chemical work we are only concerned with relative weights, and therefore any inequalities in the lengths of the two arms of the beam are of no importance. When necessary, the ratio of the lengths of the arms can be obtained, and also, assuming that the weights are accurate, the true weight of the body, by using Gauss's method. The body is first weighed in the left pan (apparent weight say  $X$ ) and then in the right pan (apparent weight say  $Y$ ) ; if  $L$  and  $R$  are the lengths of the arms and  $M$  the true weight of the body, by taking moments about the centre of the beam in the two cases :

$$M \times L = X \times R \text{ and } Y \times L = M \times R$$

whence

$$L^2/R^2 = X/Y, M^2 = XY \text{ and } M = \sqrt{XY}$$

In general, no appreciable error is caused by taking

$$M = \frac{X + Y}{2}$$

The value of  $L/R$  on a good balance is usually very near to unity, say, for example, 1.00003. The value of the ratio can be altered by shifting the position of one of the knife-edges by means of the screws provided. It should be emphasized that such adjustment should only be made by a good instrument-maker. The effect of even a very small alteration in the distance causes a big error in the weighing. The difference of the apparent weight in the two scale-pans is the reason for always placing the object to be weighed in the left pan.

Another and perhaps better method of obtaining the true weight of a body is by using two sets of weights, A and B, in the following manner: Place the object on the left pan and balance it with the weights A, remove the object from the left pan and replace it by the weights B until balance is again obtained; the object and the weights B have now been balanced against the weights A under identical conditions, and the object therefore has a mass equal to that of the weights B used.

**Accurate Weighing.** The above methods of weighing are sufficiently accurate for all ordinary laboratory work; but when greater accuracy is required greater precautions must be taken to eliminate various possible errors. Those due to the disturbing effects of temperature are probably the most serious. Inequalities of temperature cause convection currents, which make it difficult to get a constant zero, or by acting on one arm of the beam more than the other may cause an object to appear heavier or lighter than it really is. In the second place, a change of temperature will alter the lengths of the two arms of the balance, and although these are constructed of the same material their expansion coefficients may not be quite the same. One effect of this is the change in the zero which takes place throughout the day. The result of a change in the ratio of the arms can be found for different temperatures and an allowance made for it when weighings are made of the same object at slightly different temperatures. This source of trouble is much aggravated by large changes of temperature, and shows the importance of a steady temperature in the balance room and of reading the temperature of the balance case each time a weighing is made or the zero determined.

Besides this gradual change of the zero a temporary change may be produced by the unequal heating of the beam by the operator's hand in loading the balance. Manley showed that within an ordinary balance case when the balance is in use there is a constant fluctuation in temperature to the extent of  $0.2^{\circ}$  in the neighbourhood of the beam. Adopting a protecting case uniformity in the temperature of the enclosed balance beam is obtained.

It is instructive for a person to try a few experiments with a sensitive balance, weighing the same object repeatedly and consecutively without altering the balance, and also to weigh the same object at different times of the day. The effect of alteration in the position of the worker in weighing can also be noticed, it being usual to get quite appreciable variations. A difference of  $0.01^{\circ}$  in the temperatures of the arms of a balance corresponds to a difference of 0.000024 per cent in the apparent weight.

**Effect of Variations in Amplitude.** If the balance is loaded and the beam released so as to swing with a large amplitude, readings can be taken of the turning-points until the pointer practically comes to rest and the R.P. can be calculated for various amplitudes. It is advisable to neglect the first



few swings, when the beam may be supposed to be in a disturbed state due to the three knife-edges not being released at exactly the same instant, and to the effect of the sudden strain on it. Irregular values of the R.P. are found with large amplitudes, but the value tends to become steady when the amplitudes do not exceed five divisions. This is most probably due to a slight lateral shift of the knife-edges, which is pronounced unless the latter are attached, as outlined above.

**Procedure in Accurate Weighing.** To obtain the weight of a substance accurately the following procedure should be adopted: The pointer is observed through a reading telescope 2 or 3 metres away from the front of the case. This enables the observer to estimate to a tenth of a scale division with fair accuracy, avoids errors due to parallax, and prevents the parts of the balance being unequally heated by radiation from the observer's person. If artificial illumination is used it should be from directly behind and above the observer. The balance case is preferably covered with a non-conducting jacket, leaving only a small aperture for the observance of the scale. The pans are dusted with a camel-hair brush kept for that purpose, the case is closed and the beam released and left to swing for 20 minutes to become thoroughly fatigued. This avoids small errors due to slight changes in the positions of the small adjusting screws on the beam. If the amplitude is then too small for observations to be made conveniently, it is increased, and after a few preliminary swings the turning-points are recorded for five or seven swings, and from these the zero is calculated. The temperature of the case is read and the barometric height is recorded.

The object to be weighed is then removed from the desiccator, wiped with a piece of silk, placed on the left-hand pan and balanced with weights. The case is closed and left for some hours. The beam is then released and allowed to swing for 20 minutes to become properly fatigued, when the R.P. is determined. The weights used should be such as to give a R.P. just greater than the zero; 1 milligram is added by means of the rider and the new R.P. is determined. The difference between the two values gives the sensitiveness; the temperature and barometric height are recorded. The object and the weights are then interchanged, and after waiting some time (a shorter time than in the first case is sufficient) the beam is released, fatigued for the usual time, and the R.P. determined; 1 milligram is added, and from the new R.P. the sensitiveness is calculated. Temperature and pressure are again recorded. Finally, after the object is removed, the zero is again determined and the temperature read. If the two values of the zero differ, owing to the temperature having altered, the value at each of the temperatures at which weighings were made is calculated, and these values of the zero are used in conjunction with the R.P.s and sensitiveness already found, to calculate the apparent weight in each pan. The two weights so obtained are corrected for errors in the weights themselves and are reduced to vacuum in the manner presently to be described; the arithmetic mean of these two weights is taken to be the true weight of the body. The time allowed for the body to remain in the case before the weighing is commenced will depend on the size and nature of the object, as has already been mentioned. In some cases better results are obtained by balancing the object with a similar tare, and in other respects proceeding as above. Noyes, in the determination of the

atomic weight of hydrogen, had occasion to weigh glass vessels containing the reagents under experiment. Before placing in the balance case the vessels were always wetted and wiped dry with a clean cloth; they were then placed in the balance pan and balanced with a piece of glass apparatus of the same size and weight. A stream of dried and filtered air was then passed through the case for from 12 to 24 hours. The air current was stopped about 20 minutes before the weighing was made. After weighing, the air current was again started and the weighing repeated after an hour. The average difference between the two weights was 0.05 milligram, while vacuum corrections had only to be applied to the weights used and for the small difference in the volume of the object and its tare. Advantage is often taken of the absence of vibration due to external causes such as trains, trams, and machinery at night, and the weighings are then made.

It is estimated that the degree of accuracy attainable ranges from 0.03 milligram to 0.006 milligram, but even the former figure is rarely attained in practice. In all cases it should be remembered that extreme accuracy in the weighing is of no value unless all the other operations involved can be carried out with accuracy of the same order; and as the balance is one of the most precise instruments available this is seldom possible. It is only in research work that any attempt to obtain accuracy to more than 0.1 milligram is necessary or desirable.<sup>1</sup>

**Vacuum Corrections.** When an object is weighed in air, both the object and the weights used, owing to the buoyancy of the air, lose weight equal to the weight of the volume of air displaced; since the weight of a given volume of air depends on the temperature, pressure, and humidity, the buoyancy of the air varies, and therefore the apparent weight of an object will also vary from day to day.

To overcome this difficulty the apparent weight of the body is corrected to what it would be *in vacuo*. Suppose the body to have a mass  $m$  and a density  $\rho$ , and the density of the air at the temperature, pressure, and humidity at the time of weighing to be  $\delta$ , the volume of the body is  $\frac{m}{\rho}$  ml., and this is also the volume of the air displaced; this air weighs  $\frac{m\delta}{\rho}$  grams, and the real weight of the body *in vacuo* is therefore  $\frac{m\delta}{\rho}$  greater than its weight in air. In the same way the weights used lose weight  $\frac{m\delta}{\rho_1}$  where  $\rho_1$  is the density of the material used in the construction of the weights; this makes the body appear lighter than it really is, so that a correction to the apparent weight must be made by adding  $\frac{m\delta}{\rho} - \frac{m\delta}{\rho_1}$ . The corrected weight *in vacuo* is therefore

$$M = m \left( 1 + \frac{\delta}{\rho} - \frac{\delta}{\rho_1} \right) = m + mR$$

where

$$R = \frac{\delta}{\rho} - \frac{\delta}{\rho_1}.$$

<sup>1</sup> Reilly and Rae, *The Scientific Amer. Suppl.*, 1916, LXXXIV.

To get an idea of the accuracy with which the different variables must be known to fix this correction we will first consider the effect of a variation of  $5^\circ$  in temperature and of 1 cm. in the height of the barometer, on the weight of an object of density near to 1. Taking the density of air to be approximately 0.0012, a change in the temperature of  $5^\circ$  will alter this by  $\frac{1}{80}$ th, so that the change in the apparent weight of 1 ml. will be  $+0.00002$  gram, while for 1 cm. change of pressure the apparent weight change will be 0.000016 gram. Should both changes occur so as to affect the weight in the same direction, the change would be 0.000036 gram per millilitre, so that in weighing to the fourth place this is not negligible for volumes of 2 ml. or more.

As already mentioned, the value of  $\delta$  depends not only on the temperature and pressure, but also on the humidity of the air in the balance case, and of these quantities the humidity is the most difficult to estimate with accuracy. Kuhn found it to be between 55 and 60 per cent, Wade and Merriman estimate it to be 50 per cent, and Brauner found it to be 35 per cent; the ordinary desiccating agents used give very variable results. The effect on the density of the air of a change of 10 per cent in the neighbourhood of a humidity of 60 per cent is 0.000001 gram per millilitre, i.e. 0.1 milligram on 100 ml., the value of  $\delta$  being given by the formula

$$\delta = \frac{0.001293}{1 + 0.00367t} \times \frac{b - 0.375e}{760}$$

where  $t$  = temperature of air in the balance case,

$e$  = the vapour tension of the water in the air,

$b$  = the height of the barometer in millimetres reduced to standard conditions.

Many writers suggest the use of 0.0012 for  $\delta$ ; this is sometimes of insufficient accuracy. In order to get the vacuum correction to 0.0001 gram in the case of an object of density about 2 and volume 100 ml. we require the value of  $\delta$  to 0.000001, and therefore to know the temperature, pressure and relative humidity to a close degree of accuracy—

$t^\circ$  to  $0.5^\circ$

$b$  „ 1 mm.

$e$  „ 10 per cent.

Table A<sup>1</sup> gives the necessary buoyancy correction for an apparent weight of 1 gram when platinum-iridium, brass, quartz or aluminium weights are employed for  $\delta$  equal to 0.0012, which is sufficiently accurate for most purposes.

As will be obvious from the table (A) it is only necessary to know approximately the density of the substance under examination. This also applies to a large extent to the density of the standard masses employed. For these masses the following densities have been taken: platinum-iridium (90 per cent Pt),  $\rho = 21.5$ ; brass,  $\rho = 8.4$ ; quartz,  $\rho = 2.65$ ; aluminium,  $\rho = 2.58$  to 2.70.

If the apparent mass of the body be  $m$ , the true mass =  $m + mR$ .

<sup>1</sup> Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 1923, Vol. 1, 14.

TABLE A

$R \times 10^3$				$R \times 10^3$			
$\rho$	Platinum-Iridium	Brass	Quartz or Aluminium	$\rho$	Platinum-Iridium	Brass	Quartz or Aluminium
0.70	+ 1.66	+ 1.57	+ 1.26	1.4	+ 0.80	+ 0.71	+ 0.40
0.72	1.61	1.52	1.21	1.5	0.74	0.66	0.35
0.74	1.57	1.48	1.17	1.6	0.69	0.61	0.30
0.76	1.52	1.44	1.13	1.7	0.65	0.56	0.25
0.78	1.48	1.40	1.09	1.8	0.61	0.52	0.21
0.80	1.44	1.36	1.05	1.9	0.58	0.49	0.18
0.82	1.40	1.32	1.01	2.0	0.54	0.46	0.15
0.84	1.37	1.29	0.98	2.2	0.49	0.40	0.09
0.86	1.34	1.25	0.94	2.4	0.44	0.36	0.05
0.88	1.31	1.22	0.91	2.6	0.41	0.32	0.01
0.90	1.28	1.19	0.88	2.8	0.37	0.29	— 0.02
0.92	1.25	1.16	0.85	3.0	0.34	0.26	— 0.05
0.94	1.22	1.13	0.82	3.5	0.29	0.20	— 0.11
0.96	1.19	1.11	0.80	4	0.24	0.16	— 0.15
0.98	1.17	1.08	0.77	5	0.18	0.10	— 0.21
1.00	1.14	1.06	0.75	6	0.14	0.06	— 0.25
1.02	1.12	1.03	0.72	7	0.12	0.03	— 0.28
1.04	1.10	1.01	0.70	8	0.10	0.01	— 0.30
1.06	1.08	0.99	0.68	9	0.08	— 0.01	— 0.32
1.08	1.06	0.97	0.66	10	0.06	— 0.02	— 0.33
1.10	1.04	0.95	0.64	12	0.04	— 0.04	— 0.35
1.15	0.99	0.90	0.59	14	0.03	— 0.06	— 0.37
1.20	0.94	0.86	0.55	16	0.02	— 0.07	— 0.38
1.25	0.90	0.82	0.51	18	0.01	— 0.08	— 0.39
1.30	0.87	0.78	0.47	20	0.004	— 0.08	— 0.39
1.35	0.83	0.75	0.44	22	— 0.001	— 0.09	— 0.40

It will be seen that the correction  $m\left(\frac{\delta}{\varrho} - \frac{\delta}{\varrho_1}\right)$  is zero when the object and the weights have the same density, and has the greatest value when  $\varrho$  and  $\varrho_1$  are widely different.

Owing to the uncertainty of the vacuum corrections it is advisable to make them as small as possible, especially when weighing objects of large volume; the use of tares in the latter case is almost universal, the only vacuum correction then required being for the difference in volume of the object and its tare, which difference is small.

With the same object the use of quartz weights for weighing glass apparatus has been suggested; these are practically unchangeable in the air, but are easily broken if accidentally dropped, while their cost puts them beyond the reach of most laboratories.

#### STANDARDIZATION OF WEIGHTS

In all exact physico-chemical work it is essential that the weights used should be standardized by having their values relatively to one another

determined. If the operations on hand only involve the ratios of the weights of bodies like a gravimetric analysis this is sufficient to obtain accurate results, but if absolute weights are in question then it is necessary to determine the absolute weight or mass of one of the set and thence deduce the true weight or mass of the remainder from the comparisons previously carried out.

New weights from a good maker will usually be found to be extremely accurate, but the changes due to wear and tear render it necessary that all weights in use be standardized at intervals of, say, six months; but the interval will, of course, depend on the amount of use they receive.

A set of scientific weights usually contains the following standard masses, reckoned in grams—50, 20, 20, 10; 5, 2, 2, 1; 0.5, 0.2, 0.2, 0.1; 0.05, 0.02, 0.02, 0.01; lower weights are obtained by the use of a rider. With such a set it is possible rapidly to obtain the weight of any body if that weight be not greater than 100 grams. Alternatively the set may be based on a 5, 2, 1, 1 unit; the former system has the advantage that the sum of the four in any unit equals the smallest in the previous unit, so that in systematic weighing, as described, an automatic check is provided at intervals. If a mistake is suspected a test can be applied by using an additional weight instead of putting back a number of weights and adding a larger one.

It is assumed in what follows that the set of weights to be standardized is of the type preferred by English makers, being based on the 5, 2, 1, 1 unit and containing, in addition, a third gram weight and also an extra centigram weight, so that all the smaller weights add up to 1 gram. The modifications necessary to standardize the other type will be sufficiently obvious. All weights of the same denomination must be distinguished from one another by suitable marks such as ', ', ', or by being stamped *a*, *b*, *c*. It is best to have the weights so stamped by the maker before they are bought, as it is unsatisfactory to scratch marks on standard weights, or to depend on small accidental differences to establish the distinction.

One of the centigram weights is placed on the left-hand pan and balanced with a tare having a mass of a little less than 1 centigram and the rider; it is necessary that the rider be not too near either end of its scale. The swing of the balance with its load is noted and then another of the centigram weights is substituted for the first, and the amount by which the rider has to be moved to obtain the same swing noted; alternatively, the method of swings may be employed. The first weight is then replaced on the left-hand pan and its weight rechecked. Each weight is compared with the other weights of the same denomination, and also with a suitable combination of the smaller weights. There are thus obtained a number of independent equations one less than the number of weights, and by assuming the value of any one of the weights the others may be calculated.

It will be noted that by always placing the weights under examination on one side of the balance any errors due to inequalities in the lengths of the arms of the balance are eliminated. Corrections for the buoyancy effect of the air are rendered unnecessary as the weights under comparison are taken all to be of the same material. Should, however, the weights below 1 gram be of aluminium and the 1 gram and above be of brass, a slight error is

introduced in the passage from one material to another, but except in very accurate work it is inappreciable.

For the purposes of calculation it is most convenient first to assume that the first weight, the smallest, is correct. The values of all the other weights in terms of this standard are then built up. While the values so obtained are consistent among themselves, they are usually far too different from the face value of the weights for convenient use, owing to the assumed standard being so small a quantity. It is necessary then to translate these consistent values into other terms by dividing each value by the value of one of the larger weights to be taken as a new and permanent standard. It is not necessary, however, to carry out this division in full. It is sufficiently accurate to compare the value of each weight with the corresponding aliquot part of the value of the weight to be taken as a final standard. The difference of the actual and ideal value will give at once the correction to be applied. Of course, if the weight is not sufficiently heavy this correction is minus and must be subtracted from the result of any weighing in which this weight is used. The table <sup>1</sup> below presents the data and result of a standardization; a few equations are given to show how the figures given are deduced, but a little practice will enable all to be written down from mental calculation. In the first column (A) the weights are named by their face values, which are enclosed in parentheses to show that they do not signify true grams. The second column (B) gives the results of the mutual comparison; the third column (C) the actual values of the weights based upon the first centigram weight. These values are obtained by adding together the appropriate preceding fractional weight enumerated in the second column. The aliquot parts of a standard 10 gram weight, which was employed to fix the real values of the weights, are recorded in the fourth column (D); while the corrections sought, obtained by simply subtracting the numbers in the fourth column from those in the third, are given in the last vertical row (E).

**Example.** Let  $(0.01)'$  gram be the centigram weight which is taken to be correct, and let the mass of the tare employed be denoted by A. Then, if a balance was obtained with the rider at 0.38 milligram  $(0.01)' = A + 0.0038$  gram. Replacing  $(0.01)'$  by  $(0.01)''$  it is found that  $(0.01)'' = A + 0.0044$  gram; hence  $(0.01)''' = (0.01)' + 0.0006$  gram. Similarly it is found that  $(0.01)'''' = (0.01)' - 0.0001$  gram.

The  $(0.01)'$  and  $(0.01)''$  gram weights are now placed upon the left-hand pan, and a  $(0.02)$  gram tare is placed on the right-hand pan. The position of the rider when balance is obtained is noted; in order that a suitable position may be obtained, a 5 milligram weight may be kept in the left-hand pan; all the tares may then be obtained by the use of a crude set of weights. The two centigram weights are replaced by the 0.02 gram weight, and the shift of the rider necessary to obtain equilibrium noted, from which the value of the weight in terms of the  $(0.01)'$  and  $(0.01)''$  gram weights, i.e. in terms of the  $(0.01)'$  gram weight, can be written down immediately. Working in this way we obtain the columns (A), (B) and (C) of the following table. The aliquot parts of the value for the 10 gram piece which is now to be taken as the permanent standard are recorded in column (D), while the corrections sought are obtained by simply subtracting the numbers in column (D) from

<sup>1</sup> Table by Richards, *J. Amer. Chem. Soc.*, 1900, 22, 147.

## PHYSICO-CHEMICAL METHODS

TABLE B

Nominal value (A)	Data obtained by substitution method (B)	Preliminary values (actual) (C)	Aliquot part of 10.01768 (ideal) (D)	Corrections in milligrams (actual minus ideal) (E)
	grams.	grams.	grams.	
(0.01)	Standard of comparison	Standard	0.01002	— 0.02
(0.01')	(0.01) + 0.00006	0.01006	0.01002	+ 0.04
(0.01'')	(0.01') — 0.00001	0.01005	0.01002	+ 0.03
(0.02)	(0.01) + (0.01') — 0.00001	0.02005	0.02004	+ 0.01
(0.05)	(0.02) + &c. — 0.00007	0.05009	0.05009	0.00
(0.1)	(0.05) + &c. — 0.00006	0.10019	0.10018	+ 0.01
(0.1')	(0.1) + 0.00001	0.10020	0.10018	+ 0.02
(0.2)	(0.1) + (0.1') — 0.00004	0.20035	0.20035	0.00
(0.5)	(0.2) + &c. — 0.00011	0.50088	0.50088	0.00
(1)	(0.5) + &c. — 0.00004	1.00183	1.00177	+ 0.06
(1')	(1) — 0.00002	1.00181	1.00177	+ 0.04
(1'')	(1) — 0.00006	1.00177	1.00177	0.00
(2)	(1') + (1'') + 0.00025	2.00383	2.00354	+ 0.29
(5)	(2) + &c. — 0.00040	5.00884	5.00884	0.00
(10)	(5) + &c. — 0.00040	10.01768	10.01768	Standard
&c.	&c.	&c.	&c.	&c.

those in column (C) and are given in column (E). If the 10 gram weight employed as a permanent standard is one which has been accurately standardized by an Institution such as the National Physical Laboratory, the corrections for all the weights give not only their relative but also their actual values.

In a modification of Richards' process by Hopkins, Zinn and Rogers,<sup>1</sup> in place of one standard being employed a special box of four standard weights—100 milligram, 1 gram, 5 gram, 50 gram—is used. This eliminates a possible objection to the use of one standard only in that, in the process of redistribution of errors, as described by Richards, a compensation of errors might occur so that a weight on which there was no correction might be assigned a positive or negative to which it was not entitled. The method employed is similar to that which has been described, except that the weights from one standard to the next are calibrated against the higher standard.

While both the methods give results sufficiently accurate for most purposes, in practice the most satisfactory method is to compare the box of weights, weight by weight, against a box of standardized weights of similar material. All calculations and corrections are avoided in this way. The method is described in detail in *Physico-Chemical Practical Exercises*, Rae and Reilly (*Methuen*).

<sup>1</sup> *J. Amer. Chem. Soc.*, 1920, 42, 2528.

## SECTION 6: TIME

**Units of Time.** The unit of time in the metric system is the mean solar second, which is the  $\frac{1}{86,400}$ th part of the mean solar day. The latter is defined as the average interval between successive transits of the centre of the sun across any given meridian, so that the unit depends on the constancy of the rotation of the earth. This is known not to be absolutely constant, but for all practical purposes it may be taken to be so. The unit of time is thus essentially different from those of space or mass in that it cannot be compared with a reliable standard, but can only be measured by the repetition of a

In physical chemistry and in physics one is not usually concerned with the standard time, deduced from astronomical observations, at which an event occurs, but rather with the duration of a particular event, or with intervals measured from an arbitrary time-zero at which events under observation occur or at which properties under observation have a particular value.

### MEASUREMENT OF TIME

**General Considerations.** All instruments used in measuring times depend on the comparison of the progress of the operation under examination with some standard operation which is assumed to repeat itself regularly, or with some operation which is continuous, and the progress of which can readily be divided into portions of equal duration. The former principle is employed in all clocks and watches and, in fact, in most time-measuring instruments. These all contain a vibrator such as a pendulum or balance wheel which has the mechanical property of repeating its vibrations uniformly. Mechanism is provided by which the retarding effect of friction, &c., is just overcome and uniform vibration continuously maintained. The principles and methods applied to obtain such mechanisms and to compensate them for changes in temperature and the like lie outside the purview of physical chemistry.

The second method of measuring time is employed in the modern chronograph, but it is of ancient origin. Before clocks, &c., had attained their present mechanical perfection it was in frequent use; for instance, Galileo measured relative times by the amount of water flowing through an orifice under a constant head.

### INSTRUMENTS

**Intervals down to 0.003 second.** For many of the time measurements involved in physical chemistry a watch with a second-hand suffices.



In viscosity and a few other measurements a stop-watch reading to  $\frac{1}{5}$ th of a second may be employed. The metronome can also be applied, and is useful in enabling seconds to be counted accurately while the eye is employed in making the observation.

Of greater convenience are self-recording instruments in which the exact time at which an event occurs, or the time interval between two events, or the value of a property at a given time, is caused automatically to register itself. Such instruments are made ready for use by various firms. The Cambridge Scientific Instrument Co. specialize in such apparatus. In one common form of instrument for relatively long time intervals, this is accomplished by providing a cylindrical drum which is driven by clockwork and rotates on its axis uniformly, completing a rotation in, say, 24 hours. On the outside of this drum is wound a sheet of graduated paper, which is divided by lines parallel to the axis of rotation into spaces representing hours and fractions of an hour. On this drum a pointer rests, and to this latter ink, by which it marks the paper, is continuously supplied. Any deflection of the pointer from its normal position will at once be apparent and such deflection can by suitable devices be caused to be reproduced by the occurrence of an event. For example, the pointer may also function as the needle of a galvanometer, and any change in the current flowing through the latter will be indicated on the paper by a movement of the needle. In this way the time between which make and break of a circuit occur, and thus the time between events which cause this make and break, can readily be measured. Again the paper can be graduated at right angles to the motion of the pointer, and the value of some quantity continually measured by the amount of the deflection. Thus we may connect a thermocouple in circuit with a galvanometer needle which also forms the pointer of a time recorder and thus obtain a continuous record of a temperature by the deflection produced, which may previously be standardized. In very accurate instruments the friction of the registration pen against the paper may cause a lag in the variations of the pointer; this is avoided by preventing the pen of the latter from continuously touching the paper, but causing it to be pressed down on the paper for a few seconds every minute or half-minute by suitable clock-work mechanism.

Figs. 40 (II) and 41 (II) show two such instruments.<sup>1</sup> The drum is driven by clockwork, and the pointer, which is a portion of a moving-coil galvanometer, swings over the surface of the drum, which carries a chart. A thread impregnated with ink passes between the pointer and the chart and once or twice a minute the pointer is automatically depressed so that it forces the inked thread down on to the chart, thus causing a mark which indicates its position, and thus the value of a temperature under test.

In other instruments for taking the value of a property which is varying rapidly, two pointers and a quickly rotating drum are employed. One pointer marks seconds on the drum; the other, which is simultaneously worked by electrical means, indicates the value of the property under measurement. Alternatively (Fig. 42 (II)) a long strip of paper is caused to pass at a uniform rate from a drum underneath the pointers, thus allowing

<sup>1</sup> The Cambridge Instruments Co., Ltd., have kindly lent electros for Figs. 40 (II)-43 (II).

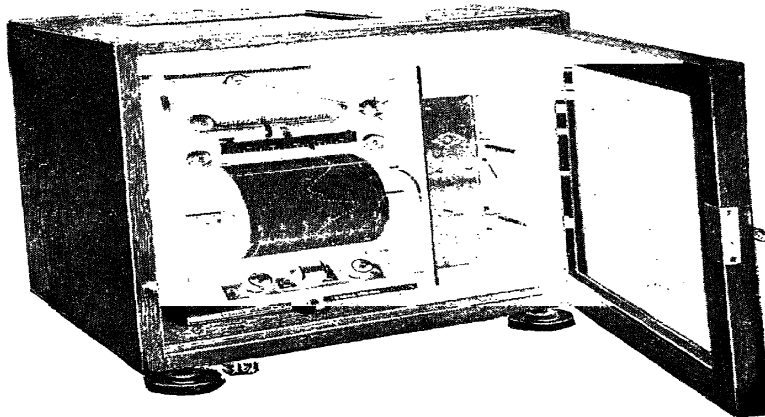


FIG. 40 (II)

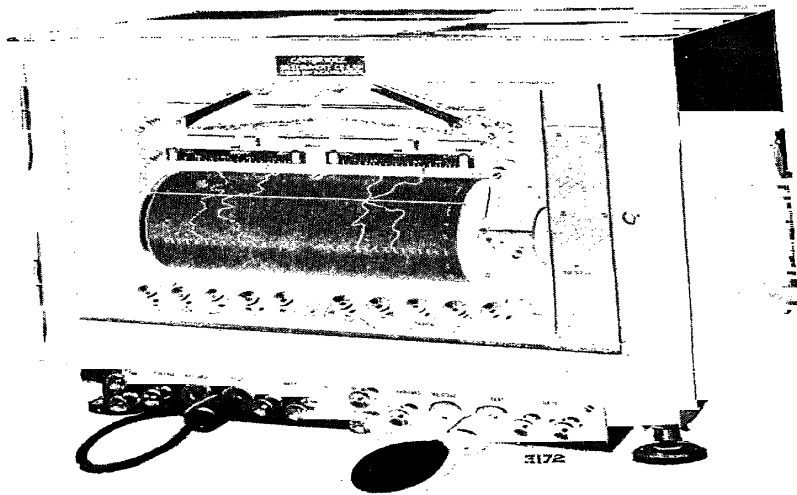


FIG. 41 (II)

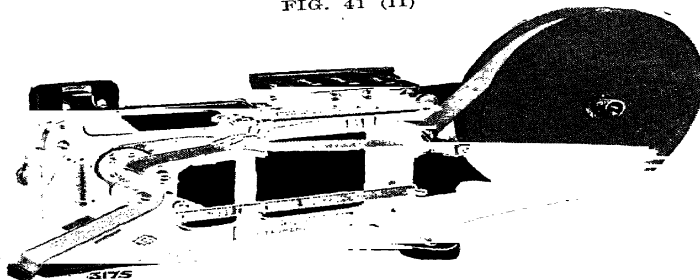


FIG. 42 (II)

a longer period for observations. The marking of seconds on the moving paper may be achieved by means of a pendulum with a period of two seconds, which at the lowest portion of its amplitude makes an electrical connection which energizes a magnet and causes a bar fixed at one end, and carrying a pen fed automatically with ink at the other, to give a sharp vibration. This causes a kink in the line which normally the pen traces on the moving paper; the interval between two such kinks represents a second. A similar bar with a pen fixed to it is moved when a current passes through a second circuit; the passage of this current depends on the occurrence of an event, for example, on the arrival of a falling body at a definite point, and so on. Chronographs are also available where the pens are removed from the paper normally and only make a mark every second and when an event occurs. In these instruments intervals of the order of  $\frac{1}{1000}$ th of a second can be determined. In other types of instruments, by means of a tuning fork or a flexible metallic bar fixed at one end, the pen is made to vibrate in contact with a rotary drum or moving strip. A wavy line is obtained where it cuts the line given by the pen at rest, and the paper is divided into lengths, corresponding to half the period of the vibrator. Owing to friction between the pen and the drum this method is not recommended for accurate work, unless

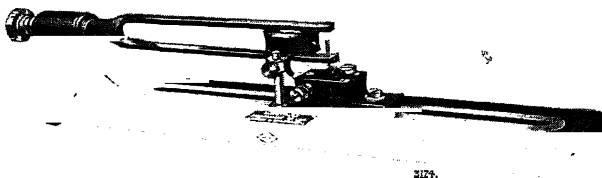


FIG. 43 (II)

electromagnetic means be provided for maintaining the vibrations of the tuning fork as shown (Fig. 43 (II)). When that is the case tuning forks making up to 200 vibrations a second can be employed. If the cylinder be caused to rotate on a screw so that it progresses uniformly along its axis while rotating, a continuous record can be obtained over a long time interval in any of the above types of apparatus.

Machines as described above find application in mechanics, Atwood's machine, which is employed to demonstrate the laws of falling bodies, &c., being an example of the kind. Here a strip of paper attached to the falling body passes underneath a pen attached to a flexible vibrating metallic bar.

A continuous record can also be obtained by causing the pointer to move uniformly along the rotating drum. In all these instruments the rotation of the drum or drums employed is accomplished by clockwork or by an electrical motor. The latter is to be preferred, for in the ordinary rotating drum chronograph the inertia of the moving parts is great in comparison with the driving power of the clockwork, and there is a tendency to irregularity of motion. In the Mond and Wildermann chronograph (Fig. 44 (II)) which is driven by clockwork this defect is overcome. The drum is fixed and the marker rotates around it; the same marker is used to indicate both the calibrating time signals and the signals to be recorded; marks of different

lengths being used for the two purposes. Horizontal and vertical types of this new instrument may be employed. The cylinder is 60 cm. in circumference and the marker can be made to rotate in 10 seconds or 1 minute,

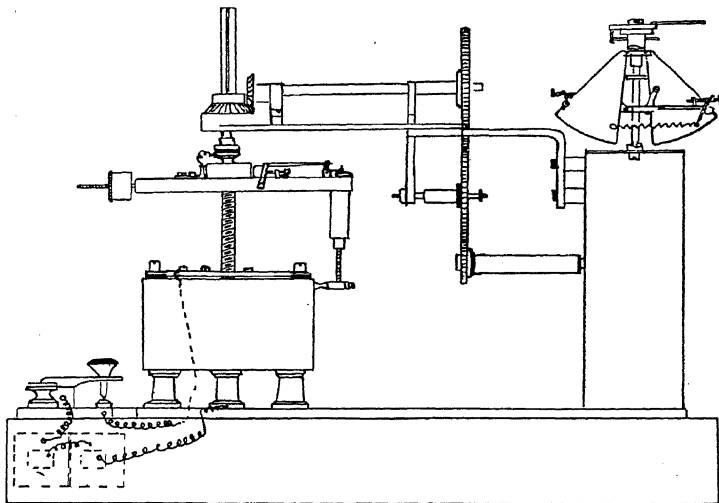


FIG. 44 (II)

fifty turns in all being possible in passing from one end of the drum to the other. Great regularity of motion is achieved and intervals of down to  $\frac{1}{300}$ th of a second can be recorded.

**Intervals down to 0.0002 second.** Still smaller intervals are given by the use as a pointer of a beam of light, which is reflected on to light sensitive

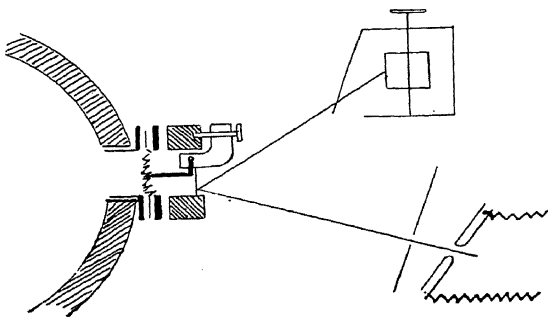


FIG. 45 (II)

paper on a very rapidly rotating drum. The mirror is arranged to move with alteration in the quantity being measured. For instance, in the membrane manometer of Pier <sup>1</sup> (Fig. 45 (II)) a concave mirror was attached to a pres-

<sup>1</sup> *Zeitsch. Elektrochem.*, 1909, 15, 536.

sure-registering membrane and a beam of light reflected by this mirror from an arc lamp on to a rotating drum covered with sensitized paper; this drum was rotated by an electric motor twice in a second, and was of such a size that a millimetre on the surface had a value of 0.00078 second. In such instruments the sensitized paper used should be as thick as possible to minimize the risk of alteration in the length of the paper on development.

By rotating the drum still faster 1 mm. can be made to represent as small a quantity as 0.0002 second, which surface graduation was obtained by Reichenstein. In order to find the time value of each rotation he caused an aluminium pointer driven by clockwork to pass through the beam of light falling on the rotating drum. Each interruption of the light was marked by a gap in the photographic curve on the drum. The time of rotation of the pointer was known, from which the interval between two breaks on the curve could be calculated. The speed of rotation of such drums can always be fixed by means of rotation counters such as are employed with electric motors or dynamos.

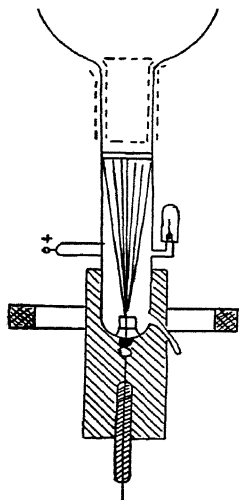


FIG. 46 (II)

**Cathode Ray Oscillograph.** Time intervals of the order of 0.0005 second can be obtained by using the cathode ray oscillograph devised by Thomson.<sup>1</sup> A stream of cathode rays is produced by a cold or hot cathode K in a highly evacuated glass tube (Figs. 46 (II) and 47 (II)). The rays are limited to a fine line by a diaphragm D, and pass on to a sensitive screen or photographic plate P. In Dufours' <sup>2</sup> arrangement a magnetic field is excited by an alternating current in the coils A and A'. Fig. 48 (II) represents the end view of the cathode stream normally impinging on the plate. This point is drawn out into a band as in *b*, by the magnetic field due to the coils A, A'. A second alternation field is produced in two coils or plates B, B<sub>1</sub>, varying with the effects it is proposed to measure. This second field acting alone would

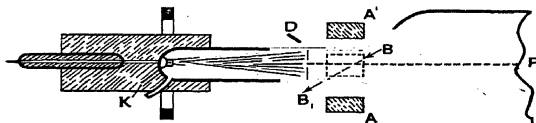


FIG. 47 (II)

produce a band *c* in the plate. If the two fields act together, and if the frequency of *b* is considerably less than that of *c*, an effect similar to that

<sup>1</sup> See Keys, *Phil. Mag.*, 1921, 42, 471.

<sup>2</sup> *Journal de Physique*, 1920, 146.

shown in *d* is obtained on the plate Fig. 48 (II). An interesting development of this has been the measurement of rapid pressure variations (due to explosions, &c.) in which use is made of the piezo electric properties of substances like tourmaline or Rochelle salt. When subjected to pressures in certain directions, these crystals exhibit a difference of polarity. On

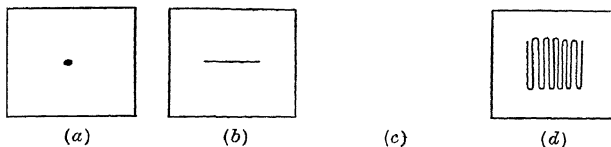


FIG. 48 (II)

joining those parts at which difference of pressure is produced to the plates B of the oscillograph pressure changes are indicated by deflections of the cathode beam. A pressure time relation is photographically obtained by imposing on the rays a varying magnetic field of known frequency, excited by an alternating electric field in the coils A, A<sup>1</sup>, at right angles to the field produced by the pressure changes.

A chronograph with an accuracy of time measurement of 0.0002 second has been described by Sears and Tomlinson.<sup>1</sup> For details of working the original paper should be consulted. The chronograph record is driven by a simple friction coupling and two steel discs carrying the record plate. This record takes the form of two parallel spirals traced on a thin smoke film on the surface of a rotating glass plate. Two markers traverse slowly in a radial direction across the record and are propelled by the rotation of a screw. One of the spirals records seconds and the other registers required intervals of time. The speed of rotation of the drum is six revolutions per minute. The mean length of the record traced corresponds to 1 second for every 2 inches. With a suitable smoke film a line of such fineness can be traced that it is possible to set the time mark in coincidence with the cross hair to within 0.0001 second.

**Preparation of Smoke Film.** The glass plate is very thinly smoked by spinning over a lighted taper. A pool of petrol with a trace of vaseline in solution is then allowed to flow all over the film. The plate is then placed on edge to drain and dry. On such a film clear lines 0.0001 inch in width can be traced.

**Shorter Time Intervals.** To measure shorter time intervals recourse must be had to electromagnetic methods. More than sixty years ago Helmholtz used a horizontal magnetic pendulum for determining the duration of an electric impulse. The apparatus was in the form of a Thompson galvanometer, and the angular deviation of the magnet from its position of rest was taken as a measure of the duration of the impulse sent through the galvanometer.

**Klopsteg Impulse Counter.**<sup>2</sup> An electromagnet energized by direct current from a low voltage source operates on a pivoted armature normally held against a stop by spring tension. To the armature is attached a driving-

<sup>1</sup> *J. Sci. Inst.*, 1931, 8, 21.

<sup>2</sup> *J. Opt. Soc. of Amer.*, 1929, 19.

pawl which, at each stroke of the armature towards the magnet, advances a 60-toothed ratchet wheel one step. The motion of the ratchet is rendered positive by a check pawl and by a device which locks the driving-pawl when it is in its advanced position. The mechanism, by virtue of its small moment of inertia and ample actuating power, operates positively and without skips at all frequencies below 125 per second. The staff of the ratchet wheel carries a 'sweep-seconds' hand to indicate individual impulses on a 60-division dial.

Through a train of 30 to 1 reduction gear it drives an auxiliary hand on a small dial: with this combination the instrument registers individual impulses up to 1,800. A release button is provided for starting. The impulse counter may be applied to any movement which can be made to operate a make and break in the electrical circuit.

Of the many methods later used, perhaps the best is by determining either the partial discharge from a loaded condenser when short-circuited during the interval in question through a non-inductive resistance, or the fractional part of a full charge acquired by an originally empty condenser through a given non-inductive resistance when a constant electromotive is



applied throughout the charging time interval. This method can be made to yield very accurate results, even where intervals of the order of  $10^{-6}$  seconds are concerned, and can be applied in a variety of ways. For example, it has been used by Sabine to determine the time of contact of a hammer on an anvil.

FIG. 49 (II)

The problem involved, that of finding the fractional part of a full charge left on a condenser after unloading through a non-inductive resistance for  $t$  seconds, is a simple one. The apparatus is arranged in some such form as shown in the Fig. 49 (II), where  $Z$  is a battery of constant E.M.F., for example, two or three bichromate cells,  $r$  is a variable non-inductive resistance, and  $K$  is a standard condenser. If the condenser has acquired its full load  $Q$ , and the battery lead be severed at  $A$  by a rifle-ball, the condenser will discharge through the resistance  $r$  made up of  $r$  and the lead wires, until the ball cuts the second wire at  $B$ ; when the charge left on the condenser will be  $Q_t = Q_0 e^{-t/kr}$ , where  $t$  is the time taken by a bullet to travel from  $A$  to  $B$  and  $k$  is the capacity of the condenser in farads, when  $t = kr \log Q_0/Q_t$ . With the aid of a suitable ballistic galvanometer and key both  $Q_0$  and  $Q_t$  can readily be determined. In the application of this principle, however, certain difficulties are met with, and the exact design of the necessary apparatus has to be modified by the particular object in view and the circumstances in which it is to be applied.

A method has been developed by which time intervals of the order of  $10^{-10}$  seconds may be determined; it depends on the estimation of the distance a ray of light travels in the interval under observation. For example, the discharge of a condenser is made to produce an electrical spark, and the light from this spark is led by a measured path through carbon disulphide

which is rendered birefringent by the field produced by the condenser (Kerr effect). The light is then examined in a Nicol. The distance the light has to traverse to enable the phenomenon to have died away, and hence the time necessary for this to occur, can readily be determined. A distance of 80 cm. corresponds to  $4 \times 10^{-9}$  seconds; in this time the electro-optic effect is halved.

The above is an outline of some of the methods which have been adopted to measure the time intervals between or the time duration of operations or events. A number of other instruments and methods have been devised, especially in the sciences of engineering and mechanics, but for the most part they lie outside the scope of the present work.





## CHAPTER III

### MEASURES AND UNITS <sup>1</sup>

THE object of this chapter is to expound some general considerations concerning the metrical quantities in which the physicist and the physical chemist are interested. The following problems will be investigated :

- (1) The general formulae for changing units.
- (2) The relations between electrical measures.
- (3) The expression of physical equations as relations between tauto-metric products.
- (4) Heat transmission as illustrating this general principle.
- (5) The theory of molecular similarity as providing a method for co-ordinating a great number of empirical results in physico-chemistry and for expressing the variation of surface-tension, &c., with temperature.

The inclusion of this chapter in a 'practical' book is therefore justified, for practical work does not consist merely in isolated empirical measurements. The physico-chemist must also know how to manipulate and co-ordinate his numerical data. For this purpose a general consideration of metrical quantities is extremely useful. In the following pages there is very little physical theory in the ordinary sense; none of the current equations of state is examined. There is merely a brief survey of the general properties of physico-chemical quantities, and the mathematics involved is reduced to a minimum. The treatment is simple and direct; there is practically no attempt to criticize or refute existing vague ideas on 'dimensions'. The notation employed is different from that used elsewhere in the book; in particular, capital letters are largely appropriated to a special use. No real inconvenience will be caused by this procedure, which is chosen in order to make the exposition clear and concise.<sup>2</sup>

<sup>1</sup> By Professor Alfred O'Rahilly, University College, Cork.

<sup>2</sup> For example,  $T$  cannot be used to denote surface-tension ( $s$ ), for it is first used to mean the measure-ratio of time and subsequently the reduced temperature. Whether viscosity is called  $\eta$  or  $\mu$  is a matter of indifference.

## SECTION 1 : MEASURE-RATIOS

Quantitative science is concerned largely with measures or ratios such as  $l = A/B$ . Here  $l$  is a *length*, the ratio which the concrete spatial magnitude A (which we may call Length with a capital letter) bears to a conspecific magnitude (another Length) which we term the unit. The theorist deals with ratios such as  $l$ , which—though it is an ordinary number—is called a ‘physical quantity’. It is the business of the man in the laboratory to measure, i.e. to provide the number  $l$  by comparing A and B. It is to be noted that these letters, A and B, do not stand for numbers; they merely designate, or point out, the two instances of that objective spatial entity which we call Length. If we use two different units for measuring the same Length (A), we obtain two different measures :

$$l_1 = A/B_1 \text{ and } l_2 = A/B_2$$

Let L denote the *measure-ratio*, i.e. the ratio of the two measures of the same magnitude A with respect to the two units  $B_1$  and  $B_2$ . That is,

$$L = \frac{l_1}{l_2} = \frac{A/B_1}{A/B_2} = \frac{B_2}{B_1}$$

The measure-ratio is therefore the inverse or reciprocal of the units-ratio.

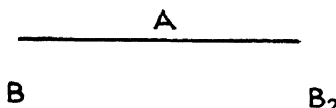


FIG. 1 (III)

It is very convenient—but by no means necessary—to introduce a third hypothetical unit C, to which for distinction we shall refer as the *standard* (Fig. 1 (III)). If  $\lambda_1$  and  $\lambda_2$  are the measures of our two units in terms of the standard,  $\lambda_1 = B_1/C$  and  $\lambda_2 = B_2/C$ . We then have

$$L = l_1/l_2 = \lambda_2/\lambda_1$$

Suppose now that we consider the measures,  $l_1'$  and  $l_2'$ , of another magnitude A' (conspecific with A) referred to the same two units  $B_1$  and  $B_2$ . Then obviously

$$l_1'/l_2' = \lambda_2/\lambda_1 = l_1/l_2 = L$$

Thus L is the ratio of the two measures of *any* of the A magnitudes relative to the two given units. So long as these two units remain the same, L is constant:  $l_1 = Ll_2$ ,  $l_1' = Ll_2'$ , &c.

Confining ourselves to mechanical quantities (measures), we see from the ordinary elementary formulae that they are all defined in terms of the three quantities: length, mass and time. For example, velocity is a measure defined by  $v = l/t$ . Suppose we change our units of these three

quantities; so that  $l_1, m_1, t_1$  become  $l_2, m_2, t_2$ , where  $l_1 = Ll_2$ ,  $m_1 = Mm_2$ ,  $t_1 = Tt_2$ . Then  $v_1$  becomes  $Vv_2$ , where

$$\frac{v_1}{v_2} = \frac{l_1/t_1}{l_2/t_2} = \frac{l_1/l_2}{t_1/t_2} = \frac{L}{T}$$

It must be clearly understood that there is nothing mysterious about these measure-ratios  $L, T, V$ . They are ordinary algebraic numbers. Sometimes indeed we may be short of capital letters, or Greek capitals may be inconvenient or liable to cause confusion. We may then use a different letter, e.g.  $D = \varrho_1/\varrho_2$  for the measure-ratio of density. Or we may use square brackets as  $[\alpha]$  for  $\alpha_1/\alpha_2$ . But, let us emphasize once more, there is nothing esoteric implied by this notation. It is also convenient to call the equation  $V = L/T$  a *logometric* formula.<sup>1</sup>

The logometric formulae for the ordinary quantities occurring in mechanics can now be written down almost automatically:

Quantity	Equation and Transformation	Logometric Formula
Area . . . .	$A_1 = x_1 y_1 = L^2 x_2 y_2 = L^2 A_2$	$[A] = L^2$
Volume . . . .	$V_1 = x_1 y_1 z_1 = L^3 V_2$	$[V] = L^3$
Density . . . .	$\varrho_1 = \frac{m_1}{V_1} = \frac{M}{L^3 \varrho_2}$	$D = M/L^3$
Angle . . . .	$\alpha_1 = s_1/r_1 = s_2/r_2$	$[\alpha] = 1$
Velocity . . . .	$v_1 = \frac{l_1}{t_1} = \frac{L}{T} v_2$	$V = L/T$
Acceleration . . . .	$a_1 = \frac{\delta v_1}{\delta t_1} = \frac{V}{T} \frac{\delta v_2}{\delta t_2} = \frac{L}{T^2} a_2$	$A = L/T^2$
Force . . . .	$f_1 = m_1 a_1 = (ML/T^2) f_2$	$F = ML/T^2$
Pressure . . . .	$p_1 = \frac{f_1}{A_1} = \frac{F}{L^2} \frac{f_2}{A_2} = \frac{M}{LT^2} p_2$	$P = M/LT^2$
Work . . . .	$w_1 = f_1 l_1 = FL f_2 l_2 = \frac{ML^2}{T^2} w_2$	$W = ML^2/T^2$
Energy . . . .	$\frac{1}{2} m_1 v_1^2 = MV^2 \frac{1}{2} m_2 v_2^2$	$W = MV^2 = ML^2/T^2$
Viscosity . . . .	force/area = $\mu dv/dy$	$E \equiv [\mu] = M/LT^2$
Surface-tension . . . .	$s$ = force/length	$S = F/L = M/T^2$
Elastic coefficient . . . .	force/area = stress = $q \times$ strain	$Q = F/L^2$

It will be observed—a theoretical reason can be adduced for the fact—that all these logometric formulae are particular cases of  $Q = L^x M^y T^z$ , where  $Q = q_1/q_2$  is the measure-ratio of the quantity  $q$ .

Let  $\lambda_1, \mu_1, \tau_1$  and  $\lambda_2, \mu_2, \tau_2$  be the measures of the two given sets of *units* of length, mass, and time in terms of a hypothetical standard set. As we have seen,  $L = \lambda_2/\lambda_1$ , and similarly  $M = \mu_2/\mu_1$ ,  $T = \tau_2/\tau_1$ . Substituting, we obtain the important general formula

$$q_1 \lambda_1^x \mu_1^y \tau_1^z = q_2 \lambda_2^x \mu_2^y \tau_2^z$$

<sup>1</sup> From  $\lambda\omicron\gamma\omicron\varsigma$  (ratio) and  $\mu\epsilon\tau\rho\omicron\nu$  (measure). It is therefore merely a more euphonious form of the adjective measure-rational; and it replaces the existing term ‘dimensional’.

Or, if there is no danger of confusion with our previous notation, we can substitute roman letters :

$$q_1 l_1^{x m_1} t_1^z = q_2 l_2^{x m_2} t_2^z \quad . \quad . \quad . \quad (1)$$

Here  $q_1$  is the measure of  $q$  in set 1 of units whose measures in the 'standard' system are  $l_1$ ,  $m_1$ , and  $t_1$ ; and similarly for the letters with the subscript 2.

Let us begin with a simple example : Express in miles per hour a speed of  $v_1$  feet per second. Since  $V = L/T$ , we have  $v_1 l_1/t_1 = v_2 l_2/t_2$ . Now  $l_1$ ,  $t_1$  and  $l_2$ ,  $t_2$  are the measures of foot, second and mile, hour, respectively, in the standard or hypothetical system of units. To particularize, let us take this third system of units to be yard and minute. We then have

$$v_1 \frac{\text{ft./yard}}{\text{sec./min.}} = v \frac{\text{mile/yard}}{\text{hour/min.}} = v_2 \frac{5,280 \text{ ft./yard}}{3,600 \text{ sec./min.}}$$

We then cancel the factor

$$\frac{\text{ft./yard}}{\text{sec./min.}}$$

which is an ordinary number, and obtain

$$v_2 = \frac{60}{88} v_1$$

This simple example shows us that it is unnecessary to specify the standard system, which may be left quite arbitrary. We therefore resolve to abbreviate our notation and to write 'ft.' instead of ft./yard, and so on. So we have

$$v_1 \frac{\text{ft.}}{\text{sec.}} = v_2 \frac{\text{mile}}{\text{hour}} = v_2 \frac{5,280 \text{ ft.}}{3,600 \text{ sec.}}$$

or

$$v_1 = \frac{88}{60} v_2$$

It may seem an unnecessary refinement to drag in this hypothetical system of units (such as yard and minute). But unless we do so, we shall be talking nonsense. How else shall we give a meaning to the expression ft./sec., which is an ordinary number multiplying  $v_1$  and  $v_2$  and is accordingly cancelled as a common factor? But, having once justified his procedure, the student need have no further explicit advertence. He can without scruple write down

$$v_1 \frac{\text{cm.}}{\text{sec.}} = v_2 \frac{\text{km.}}{\text{hr.}} = v_3 \frac{\text{mile}}{\text{hr.}} = v_4 \frac{\text{ft.}}{\text{sec.}} = \&c.$$

and at once obtain

$$v_1 = 27.78 v_2 = 3.725 v_3 = 30.48 v_4 = \&c.$$

Changing units becomes a very simple process.

Let us take some examples.

(1) The flow of water, in cubic feet per minute, through a right-angled notch is given by  $q_1 = 0.305 h_1^{3/2}$ , where  $h_1$  is the head in inches above the

end of the notch. Express the flow in cubic metres per hour in terms of the head in centimetres. We have

$$\frac{q_2}{h_2^{\frac{5}{2}}} \cdot \frac{\text{metre}^3/\text{hour}}{\text{cm.}^{\frac{5}{2}}} = \frac{q_1}{h_1^{\frac{5}{2}}} \cdot \frac{\text{ft.}^3/\text{min.}}{\text{in.}^{\frac{5}{2}}}$$

$$= 0.305 \left( \frac{\text{metre}}{3.28} \right)^3 \times \frac{1}{\text{hr.}/60} \times \frac{1}{(2.54 \text{ cm.})^{\frac{5}{2}}}$$

Cancelling the common factor, we find at once

$$q_2 = 0.0504 h_2^{\frac{5}{2}}$$

(2) How many watts in a horse-power? The logometric formula for power is  $FV$  or  $ML^2/T^3$ . A watt is  $10^7$  ergs per second, a horse-power is 550 ft.-lb. per second. A kilo weighs 2.2046 lb., hence 1 gram contains  $(2.2046/1,000 \times 32.2)$  engineers' unit of mass. Omitting the factor  $1/\text{sec.}^3$ , we have

$$q \times 10^7 \text{ gram} \times \text{cm.}^2 = 550 (\text{eng. unit}) \times \text{ft.}^2$$

$$= 550 \times \frac{1,000 \times 32.2}{2.2046} \text{ grams} \times (12 \times 2.54 \text{ cm.})^2$$

Whence

$$q = 746.$$

(3) Given that the mechanical equivalent of heat in C.G.S.—Centigrade units is  $4.18 \times 10^7$ , find its value in foot-pound-second-Fahrenheit units. We take heat<sup>1</sup> as measured by mass of water  $\times$  change in temperature:  $h = m\theta$ . The mechanical equivalent of heat ( $j$ ) is given by:  $j\dot{h} = \text{work}$ . Hence  $J = L^2/\Theta T^2$ . Putting  $t_1 = t_2$ , since we measure in seconds in both systems, we have

$$4.18 \times 10^7 \times \frac{\text{cm.}^2}{\text{Cent.}} = j_2 \frac{\text{ft.}^2}{\text{Fahr.}}$$

$$= j_2 \frac{(\text{cm.} \times 12/0.3937)^2}{\text{Cent.} \times 5/9}$$

Whence

$$j_2 = 24996.1$$

Now  $j_1$  is the ergs necessary to raise 1 gram of water through  $1^\circ$  Centigrade, so that  $j_2$  is the ft.-lb. required to raise 1 engineers' unit of mass through  $1^\circ$  Fahrenheit. But in practice what is—conveniently but inconsistently—used is  $j_3$  = the ft.-lb. necessary to raise 1 lb. (i.e. the mass of water weighing 1 lb. in London) of water through  $1^\circ$  Fahrenheit. That is,

$$j_3 = j_2/32.2 = 776.2$$

(4) The amount of heat passing per unit surface per unit of time per degree difference of temperature is  $q_1$  when the calorie, cm., sec., and degree Centigrade are taken as units. Find its measure ( $q_2$ ) when the British Thermal Unit, the foot, the hour, and the degree Fahrenheit are taken as units.<sup>2</sup> We have

$$q_1 \cdot \frac{\text{cal.}}{\text{cm.}^2 \text{ sec. Cent.}} = q_2 \cdot \frac{\text{B.T.U.}}{\text{ft.}^2 \text{ hr. Fahr.}}$$

<sup>1</sup> The measure-ratio of heat is discussed later on (p. 100).

<sup>2</sup> It is shown on p. 101 that B.T.U. = 252 cal.

Hence

$$\begin{aligned} q_1 &= \frac{\text{B.T.U.}}{\text{cal.}} \cdot \left( \frac{\text{cm.}}{\text{ft.}} \right)^2 \cdot \frac{\text{sec.}}{\text{hr.}} \cdot \frac{\text{Cent.}}{\text{Fahr.}} \\ &= 252 (0.0328)^2 \cdot \frac{1}{60^2} \cdot \frac{9}{5} \\ &= 1.356 \times 10^{-4}. \end{aligned}$$

(5) Using C.G.S. units and absolute temperature (Centigrade + 273.09), we have the equation for one gram-mol ( $w$  grams where  $w$  is the molecular weight) of a gas:

$$pv = r\theta + B/v + C/v^2 + \dots$$

Let  $v_0$  be the volume in millilitres which a mol of the gas occupies at  $0^\circ$  ( $\theta_0 = 273.09$ ) under a pressure of 1 atmosphere ( $p_0 = 1.01320 \times 10^6$  dyne per sq. cm.). That is,

$$p_0 v_0 = r\theta_0 + B_0/v_0 + C_0/v_0^2 + \dots$$

Let  $u_0$  be the theoretical ideal normal volume, i.e. the volume which a mol of the gas would occupy at  $0^\circ$  and 1 atm. if it were an ideal gas obeying the law  $pv = r\theta$ . That is,

$$p_0 u_0 = r\theta_0$$

Dividing these two equations, we have

$$\begin{aligned} v_0/u_0 &= 1 + B_0'/v_0 + C_0'/v_0^2 + \dots \\ &= \text{say, } 1 - K \end{aligned}$$

$K$  can be determined from the coefficient of compressibility (at constant temperature), for

$$1/\beta_0 = -1 \left( \frac{1}{v} \frac{dv}{dp} \right)_0 = 1 + B_0/v_0^2 + 3C_0/v_0^3 + \dots$$

And if  $(pv)_0$  refers to  $0^\circ$  and small pressure and therefore large volume so that the terms in  $1/v$ ,  $1/v^2$ ,  $\dots$  are negligible,

$$(pv)_0 = r\theta_0$$

That is,

$$p_0 v_0 / (pv)_0 = 1 - K$$

If  $L$  is the mass of a 'normal litre', i.e.  $10^3 L$  is the density ( $\rho_0$ ) of a gas at  $0^\circ$  and 1 atm., the volume of a gram-mol is  $v_0 = w/\rho_0$  where  $w$  is the molecular weight. Hence

$$\begin{aligned} w &= 10^{-3} L \rho_0 \\ &= 10^{-3} u_0 (1 - K) \end{aligned}$$

For oxygen

$$w = 32, L = 1.42892, K = 956 \times 10^{-6}$$

Hence

$$u_0 = 22,416$$

and

$$\begin{aligned} r &= p_0 u_0 / 273.09 \\ &= 83.166 \times 10^6 \end{aligned}$$

(6) For 1 gram of gas

$$pv = r_1 \theta + B/v + C/v^2$$

where  $r_1 = r/w$  and  $v$  now denotes the volume of 1 gram at  $\theta$  abs. and pressure  $p$ . Leaving the measure of temperature unchanged ( $\Theta = 1$ ), let us measure the pressure in atmospheres (i.e.  $p' = p/p_0$ ) and the volume in terms of the specific volume (volume/mass) at  $0^\circ$  and 1 atm., i.e.  $v' = v/v_0$  (where  $v_0$  is our former  $v_0$  divided by  $w$ ). The new equation is

$$PVpv = Rr_1\theta + [B]V^{-1}B/v + [C]V^{-2}C/v^2$$

Since it is homogeneous, all the logometric factors are equal; and when they are divided off, the equation becomes

$$p'v' = r'\theta + B'/v' + C'/v'^2$$

We have

$$\begin{aligned} P &= p'/p = 1/p_0, & V &= v'/v = 1/v_0 \\ r'/r_1 &= R = PV = 1/p_0v_0 \\ B'/B &= [B] = PV^2 = 1/p_0v_0^2 \\ C'/C &= [C] = PV^3 = 1/p_0v_0^3 \end{aligned}$$

Suppose we wish to effect the same change of units in the equation of van der Waals:

$$(p + a/v^2)(v - b) = r_1\theta$$

Clearly

$$A = PV^2, \quad B = V, \quad R = PV$$

Hence

$$r' = r_1/p_0v_0, \quad b' = b/v_0, \quad a' = a/p_0v_0^2$$

It is more usual for experimental results to be given in the system of units which we have designated by dashed letters. By definition  $v' = 1$  when  $p' = 1$  and  $\theta = 273$ . Hence

$$(1 + a')(1 - b') = 273r'$$

Let us utilize the numbers which van der Waals calculated for carbon dioxide ( $w = 44$ ) from this formula and the measurements of Andrews:

$$r' = 0.0036865, \quad a' = 0.00874, \quad b' = 0.0023, \quad v_0 = 505.$$

Whence

$$\begin{aligned} a &= a'p_0v_0^2 = 2.25934 \times 10^9 \\ b &= b'v_0 = 1.1615 \\ r_1 &= r'p_0v_0 = 1.8871 \times 10^6 \\ r &= wr_1 = 83.03 \times 10^6 \end{aligned}$$

(7) Similarly, leaving the measures of temperature and time unchanged ( $T = \Theta = 1$ ), we can find the measure-ratios of  $r_1$ ,  $a$ ,  $b$  in terms of those of pressure ( $P = M/L$ ) and density ( $D = M/L^3$ ):

$$\begin{aligned} R &= ML^2 = P^{\frac{1}{2}}D^{-\frac{1}{2}} \\ A &= ML^5 = P^4D^{-3} \\ B &= L^3 = P^{\frac{1}{2}}D^{-\frac{1}{2}} \end{aligned}$$

Hence taking atm.-sp. vol.-sec.-grad. as our system of units, i.e.  $P = 1/p_0$  and  $D = v_0$ , we have

$$r_2 = r_1/p_0^{\frac{1}{2}}v_0^{\frac{3}{2}}, \quad a_2 = a/p_0^4v_0^3, \quad b_2 = b/p_0^{\frac{1}{2}}v_0^{\frac{3}{2}}$$

That is, in this system denoted by the suffix 2, the equation is

$$(p_2 + a_2/v_2^2)(v_2 - b_2) = r_2\theta$$

(8) The C.G.S. unit of viscosity is called a *poise* (after the Frenchman



Poiseuille) and one-hundredth of this is called a *centipoise*, which is very approximately the viscosity of water at 20°. How many centipoises are there in the British engineering unit of viscosity? From the definition

$$\text{force/area} = \mu \times \text{gradient of velocity}$$

That is,

$$F/L^2 = [\mu]/T$$

or

$$[\mu] = M/LT$$

Hence

$$\mu_1 \frac{\text{gram}}{\text{cm. sec.}} = \mu_2 \frac{\text{mass of 1 lb.}}{\text{ft. sec.}}$$

Using  $g$  for 32.2 (or 32 approx.), we have

$$\begin{aligned} \mu_2/\mu_1 &= \frac{\text{gram}}{\text{mass of 1 lb.}} \cdot \frac{\text{ft.}}{\text{cm.}} \\ &= \frac{2.2046}{1,000 \times g} \times 30.48 \\ &= 0.0672/g \end{aligned}$$

Engineers however take the unit to be  $g$ -times what it would be if the unit of force were 1 lb. That is,

$$\mu_2 = 0.0672\mu_1$$

where  $\mu_2$  is the measure of viscosity in this new unit. In other words, the British engineering unit is 1,488 centipoises.<sup>1</sup>

<sup>1</sup> Similarly instead of density ( $\rho$ ) engineers use  $w = g\rho$  (weight in lb. per c. ft.). Of course we can avoid this complication by taking 'pound' as the unit of *mass*, whose weight is then  $g = 32.2$  ('poundals'). This is what non-engineering textbooks of physics do. But against this lie serious objections: (1) Every engineer takes lb. as force, e.g. pressure as lb. per sq. in. and energy as ft.-lb. (2) James Thomson's 'poundal' is never used outside the aforesaid textbooks and causes endless confusion to engineers. (3) An engineering system is essentially based on force (just as continental engineers take kg. as weight), mass being weight/ $g$  ( $m = W/g$ ). (4) Why then duplicate the scientific mass-system (C.G.S.), especially when the British Act defining lb. specifies weight? (5) In either method consistency is unattainable, for even poundalists must use foot-pounds.

# ERRATUM (page 82)

For mass of 1 lb. read eng. unit of mass

PHYSICO-CHEMICAL METHODS I

## SECTION 2: TAUTOMETRIC PRODUCTS

In example (3) the measurement of temperature-interval occurred. For mechanics we may call the units of length, mass, and time *basic* units. It is obvious that in heat problems we must regard the unit of temperature as a fourth basic unit, independent of the other three. But in mechanics we have only three basic quantities,  $l, m, t$ ; any other quantity ( $q$ ) can be expressed in terms of these and its measure-ratio is given by  $Q = L^x M^y T^z$ . We shall call  $q$  a *derived* quantity. Since

$$p_1/p_2 = P = Q/L^x M^y T^z = 1$$

it follows that  $p_1$  and  $p_2$  have the same measure in both systems of units. More generally, if  $q_1, q_2, q_3$  are derived quantities, the product

$$p = q_1^x q_2^y q_3^z$$

is said to be *tautometric*<sup>1</sup> ('dimensionless') if  $P = 1$ . Since  $p^{\frac{1}{x}}$  is also tautometric, it will generally be convenient to express such products in the form

$$q_1/q_2^a q_3^b \quad (a = -y/x, b = -z/x)$$

As an example we may instance  $f/\rho v^2 l^2$ , where  $f$  is a force,  $\rho$  density,  $v$  velocity,  $l$  a length. In this case

$$P = \frac{ML/T^2}{ML^{-3}(LT^{-1})^2 L^2} = 1$$

so that  $p_1 = f_1/\rho_1 v_1 l_1^2$  and  $p_2 = f_2/\rho_2 v_2 l_2^2$  have the same measure. That is,  $p \equiv f/\rho v^2 l^2$  is independent of the system of units employed—provided it is employed consistently.

For the purpose of proving the following simple theorems, it is convenient to change the notation, using  $X_1, X_2, X_3$ , instead of  $L, M, T$ . If a fourth basic unit is required, the corresponding measure-ratio can be called  $X_4$ .

(1) In general, four derived quantities depending on three basic form one tautometric product.

Let  $q_1, q_2, q_3, q_4$  be the four derived quantities. We have four equations expressing the measure-ratios

$$Q_1 = X_1^{a_{11}} X_2^{a_{12}} X_3^{a_{13}}$$

$$Q_4 = X_1^{a_{41}} X_2^{a_{42}} X_3^{a_{43}}$$

Let us assume that

$$Q_4 = Q_1^l Q_2^m Q_3^n$$

<sup>1</sup> From *ταυτόν* (same) and *μέτρον* (measure). This must not be confused with the term *tautomeric* of organic chemistry (*μέρος* = part).

Substitute for the  $Q$ 's their values in terms of  $X_1, X_2, X_3$ , and equate the indices. We have at once

$$\begin{aligned}a_{41} &= a_{11}l + a_{21}m + a_{31}n \\a_{42} &= a_{12}l + a_{22}m + a_{32}n \\a_{43} &= a_{13}l + a_{23}m + a_{33}n\end{aligned}$$

To solve these equations for  $l, m$ , and  $n$  is only a matter of elementary algebra. It is convenient to use the notation of determinants. Let

$$\Delta \equiv \begin{vmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{vmatrix}$$

Then

$$l = \frac{1}{\Delta} \begin{vmatrix} a_{41} & a_{21} & a_{31} \\ a_{42} & a_{22} & a_{32} \\ a_{43} & a_{23} & a_{33} \end{vmatrix}$$

with similar expressions for  $m$  and  $n$ . Hence

$$Q_4/Q_1^l Q_2^m Q_3^n = 1$$

That is,  $q_4/q_1^l q_2^m q_3^n$  is tautometric.

(2) The condition that three derived quantities, depending on three basic, form a tautometric product, is  $\Delta = 0$ .

The previous solution fails when  $\Delta = 0$ . Let

$$\begin{aligned}Q_1 &= X_1^{a_{11}} X_2^{a_{12}} X_3^{a_{13}} \\Q_2 &= X_1^{a_{21}} X_2^{a_{22}} X_3^{a_{23}} \\Q_3 &= X_1^{a_{31}} X_2^{a_{32}} X_3^{a_{33}}\end{aligned}$$

Assuming  $Q_1 = Q_2^a Q_3^b$ , and equating indices as before, we have

$$\begin{aligned}a_{11} &= aa_{21} + ba_{31} \\a_{12} &= aa_{22} + ba_{32} \\a_{13} &= aa_{23} + ba_{33}\end{aligned}$$

Eliminating  $a$  and  $b$ , we find  $\Delta = 0$ . This therefore is the condition that  $q_1/q_2^a q_3^b$  should be tautometric.

(3) The condition that three derived quantities, depending on three basic, can be used as a probasic set, is  $\Delta \neq 0$ .

This is merely another way of stating (1). For we have there proved that if  $q$  is any fourth quantity we can express  $q$  as  $cq_1^l q_2^m q_3^n$ , provided that the determinant formed by the logometric indices of the three quantities is not zero. That is, assuming this condition, we can express the measures of all other quantities in terms of  $q_1, q_2, q_3$  instead of expressing them in terms of the basic quantities  $x_1, x_2, x_3$ . Hence  $q_1, q_2, q_3$ , which can serve as substitutes for the basic quantities, may be called a *probasic* set. For example, velocity, acceleration and energy can be used as probasic. Their measure-ratios are

$$V = LT^{-1}M^0 \quad A = LT^{-2}M^0, \quad W = L^2T^{-2}M$$

so that

$$\Delta \equiv \begin{vmatrix} 1 & -1 & 0 \\ 1 & -2 & 0 \\ 2 & -2 & 1 \end{vmatrix} = -1$$

Hence the measure-ratio of any other mechanical quantity can be

expressed in terms of  $V, A, W$ . For instance, force :  $F = V^{-2}AW$ . Similarly in hydrodynamical problems,  $\varrho, v, l$  (density, velocity, length), can be taken as probasic instead of the basic  $l, m, t$ .

(4) The following result is now obvious : In general (i.e. provided we can select three probasic), from  $n$  derived quantities depending on three basic,  $n - 3$  tautometric products may be formed.

(5) It is easy to see that these results can be extended to the case of four basic quantities. For example : In general,  $n - 4$  tautometric products can be formed from  $n$  derived quantities.

We shall next explain the important practical principle of logometric homogeneity. Suppose we have a general equation

$$f(l_1, m_1, t_1; l_2, m_2, t_2; \dots) = 0$$

which holds in any consistent set of units. That is,

$$f(Ll_1, m_1, t_1; Ll_2, m_2, t_2; \dots) = 0$$

for *all* values of the multiplier  $L$ . This can be true only if some power of  $L$  is a factor, so that

$$f(Ll_1, \dots) = L^x f(l_1, \dots)$$

Similarly for  $M$  and  $T$ . Hence

$$f(Ll_1, Mm_1, Tt_1 \dots) = L^x M^y T^z f(l_1, m_1, t_1, \dots)$$

That is, each term has the same measure-ratio. As is well known, this principle serves as a check on the accuracy of algebraic work.

If we have a general equation between  $n$  quantities, we can, by dividing by one of the terms, always introduce unity as one term and thus express the equation in the form

$$f(q_1, \dots, q_n) = 1$$

And if the relation is independent of the units employed,

$$f(q_1, \dots, q_n) = f(Q_1 q_1, \dots, Q_n q_n) = 1$$

In other words,  $f$  is a tautometric function, having the value unity for all sets of units. Now it is easy to see, without using any elaborate mathematics, that a tautometric function must be a function of tautometric products. Since each term in the original equation has the same measure-ratio, it must have been made tautometric when we divided by one of the terms. That is, we can express any general physical equation in the form

$$\phi(p_1, \dots, p_n) = 1 \quad \dots \dots \dots (2)$$

where  $p_1, \dots, p_n$  are the  $n - 3$  tautometric products formed by the  $n$  quantities. (If there were  $r$  basic quantities, the number of tautometric products would be  $n - r$ .)

Consider, for example, a hydrodynamical system in which the force ( $f$ ) on a body depends on the size (spatial length  $l$ ), the velocity ( $v$ ), the viscosity ( $\mu$ ) and the density ( $\varrho$ ), so that

$$F(f, l, v, \mu, \varrho) = 1$$

Forming the two tautometric products, with  $\varrho, v, l$  as probasic, we can express this in the form

$$\phi(p_1, p_2) = 1$$

where  $p_1 = f/\rho v^2 l^2$  and  $p_2 = \mu/\rho v l$ . Or, in other words, we know that

$$f/\rho v^2 l^2 = F(\mu/\rho v l) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

apart from any special theory determining the form of the function  $F$ . In the case of a slow-moving sphere, putting  $l = r$  and taking  $v$  to be the terminal velocity, we can take  $F = C\mu/\rho v r$ , where  $C$  is a constant. That is,

$$f = C\mu r v$$

Stokes<sup>1</sup> (in 1850) showed that  $C = 6\pi$ .

Let us express equation (3) in a slightly different notation. Put  $l = r$ ,  $A = \pi r^2$  (the cross-section); and put the tautometric product  $\rho v r/\mu = R$ , 'Reynolds's number'.<sup>2</sup> We then have

$$f/\rho v^2 A = \phi(R) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We can now subjoin some observations which have a significance for other cases besides that of a sphere moving in a liquid.

(1) The criterion for Stokes's special case is not that of 'slow motion', i.e. small  $v$ . Since by altering our units we can in any given case make the measure  $v$  as numerically large as we please, it is clear that, taken literally, this specification has no meaning. A tautometric product, on the other hand, is independent of the units employed. Hence the proper criterion is:  $R$  is small. For example, the sphere may be larger and the velocity greater in the case of a more viscous liquid; and  $R$  may still remain numerically small.

(2) Stokes's case is represented by

$$\phi(R) = 6/R$$

But this must be regarded as only the first term of a series such as

$$\phi(R) = 6/R.[1 + a R + b R^2 + \dots]$$

where  $a$  and  $b$  are constants.<sup>3</sup>

(3) The important point to observe is that the form of the function  $\phi$  is independent of the value of  $R$ . That is, if we plot a graph with  $f/\rho v^2 A$  as ordinates and the various values of  $R$  as abscissae, the results of all the various experiments should fall on *the same curve*, in spite of differences in the velocity and radius of the sphere or in the viscosity of the liquid. This is found to be the case.<sup>4</sup> This method of representing experimental results by plotting the functional relation between two tautometric products is of fundamental importance and of immense value in synthesizing the results of different experiments.

<sup>1</sup> The velocity  $v$  is 'terminal', i.e. the sphere is falling uniformly. If  $\sigma$  is its density (supposed greater than that of the fluid  $\rho$ ), the downward force is  $\frac{4}{3}\pi r^3(\sigma - \rho)g$ . Equating this to  $f = 6\pi\mu r v$ , we obtain

$$v = 2gr^2(\sigma - \rho)/9\mu$$

which is the formula given on p. 551 in a different notation ( $\eta$  used instead of  $\mu$ , the meanings of  $\rho$  and  $\sigma$  interchanged).

<sup>2</sup> It should be observed that engineers generally take  $R$  as  $\rho v d/\mu$ , where  $d = 2r$  is the diameter. This is also done in Section 5.

<sup>3</sup>  $a = \frac{3}{8}$ ,  $b = -\frac{19}{320}$  have been proposed. Cf. Goldstein, *Proc. Roy. Soc.*, 1929, 123A, 234 f.

<sup>4</sup> See the curve in Liebster, *Ann. Physik*, 1927, 82, 547.

(4) In all this work we have hitherto been assuming that only one length, the radius of the sphere, enters into the problem. The case would be altered if we were dealing with an ellipsoid, for then other tautometric products—such as the ratio of the axes and angles of orientation—would be involved. Such additional terms or variables we shall call *shape-ratios*. These will also occur if we take the dimensions of the vessel into account, e.g.  $S$  the ratio of the radius of the sphere to the radius of the cylindrical vessel. For this case, i.e.  $S$  not negligible as we have been assuming, A. Ladenburg<sup>1</sup> proposed the following modification of Stokes's formula:

$$\phi(R, S) = 6/R.(1 + 2.4 S)$$

Similarly R. A. Millikan,<sup>2</sup> in his experiments on oil drops falling in air, found that for accuracy we must take into account another tautometric product, namely, the ratio of the drop-radius to the mean free path of the gas-molecules.

Our interest in this problem has not been hydrodynamical but general. It serves as a concrete illustration of principles universally applicable. Generalizing our observations on the tautometric functions which occur everywhere in physics, we can say that the coefficients are of two kinds: (a) *operational factors*, e.g. resulting from integration; (b) *shape-factors*. Now, inasmuch as no large numbers are likely to originate from operations or shape in any practically relevant case, we naturally expect the occurrence of numbers not noticeably greater or less than unity. The occurrence of a large or small number—say,  $10^3$  or  $10^{-3}$ —is therefore generally a presumption that we have overlooked some other physical factor or molecular process.

We shall now make some brief remarks on Poiseuille's empirical formula, proved theoretically by Stokes (1847), concerning isothermal viscous flow. This formula is given (in different notation) on p. 542; as the proof is simple, we give it here. Consider (Fig. 2 (III)) a cylinder of fluid, of length  $dx$  and of cross-section  $A = \pi y^2$ , whose axis coincides with that of the tube. The viscous force opposing the motion is parallel to the axis and acts along the outer curved surface. It is equal to

$$\mu \text{ (area of curved surface) (velocity gradient at surface)}$$

That is,

$$(-dp)\pi y^2 = \mu(2\pi y dx)(-du/dy)$$

or the gradient of pressure

$$-\frac{dp}{dx} = -\frac{2\mu}{y} \frac{du}{dy}$$

<sup>1</sup> *Ann. Physik*, 1907, 23, 477. Cf. Liebster, pp. 550 ff. Ladenburg also proposed the factor  $1 + 3.3r/h$ , where  $h$  is the height of the cylinder. See later on in this book, p. 551.

<sup>2</sup> *Phys. Rev.*, 1923, 22, 1.

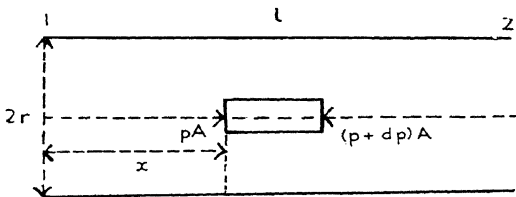


FIG. 2 (III)

Hence it is constant along the tube (independent of  $x$ ). We can therefore put

$$-dp/dx = (p_1 - p_2)/l \equiv p_{12}$$

Assuming that there is no slip ( $u = 0$  when  $y = r$ ) at the tube-wall, we have for the velocity  $u$  at a distance  $y$  from the axis

$$\begin{aligned} u &= \int_0^u du = -\frac{p_{12}}{2\mu} \int_r^u y dy \\ &= \frac{p_{12}}{4\mu} (r^2 - y^2) \end{aligned}$$

The total flow (volume flowing per unit time) is

$$\begin{aligned} q &= \int_0^r 2\pi y dy \cdot u \\ &= \frac{\pi p_{12}}{2\mu} \int_0^r (r^2 - y^2) y dy \\ &= \frac{\pi p_{12}}{2\mu} \cdot \frac{r^4}{4} \end{aligned}$$

which is the formula given (in different notation) on p. 542.

The mean velocity ( $v$ ) is defined by  $q = \pi r^2 v$ . Hence Poiseuille's formula gives

$$p_{12} = 8\mu v/r^2$$

Let us introduce two tautometric products, using the notation adopted in books on hydraulics:

$$\begin{aligned} \lambda &\equiv 4f \equiv p_{12}/(\rho v^2/2d) \\ R &\equiv \rho v d/\mu \end{aligned}$$

where  $d = 2r$  is the diameter of the tube. Then Poiseuille's formula for laminar flow is

$$\lambda = 64/R$$

But now we see at once from our previous reasoning that *in general*

$$\lambda = \phi(R) \quad \dots \dots \dots (5)$$

without resorting to any hydrodynamical argument. Moreover, we can also see that when  $R$  is small (numerically),  $\phi$  approximates to  $C/R$ , where  $C$  is a constant which we have just proved to be 64. The Poiseuille régime may therefore be defined by saying that  $R$  is small. His formula for a long time appeared to be of interest only to laboratory physicists working with capillary tubes. We see now that it is applicable to pipes of large diameter used for industrial purposes at ordinary speeds of flow, provided—as in the case of crude oil and molasses—the viscosity is relatively so high that  $R$  remains moderate (say, less than 2,000).

The tautometric product  $R \equiv \rho v d/\mu$  is called Reynolds's number, because Osborne Reynolds (1883) was the first to prove experimentally that this is the single parameter which completely specifies all the types of fluid flow in a smooth cylindrical pipe. (That is, on the assumption that the length ( $l$ ) is sufficiently long, so that the tautometric product  $d/l$  has no variable influence.) When  $R$  attains a critical value  $R_c$ —which, apart

from complications, we can take to be about 2,000—the stream-line flow becomes turbulent and eddies are produced. Poiseuille's formula then ceases to be valid, but the general formula (5) holds. We can plot a general curve connecting the two relevant tautometric products ( $\lambda$  and  $R$ ), so that the question of devising an analytical formula becomes of secondary importance. Various suggestions for such a formula, applicable to the hydraulic régime, have been made. An excellent but forgotten formula was given in 1911 by Menneret<sup>1</sup>:

$$\lambda = \phi(R) = 64/R.[1 + a(Q - 1)^n]$$

where, if  $R_c$  and  $v_c$  denote the critical values when turbulence sets in,

$$Q = R/R_c = v/v_c$$

and  $a$  and  $n$  are constants which Menneret took to be  $a = 1.413$ ,  $n = 0.735$ . When  $R = R_c$ , the formula coincides with Poiseuille's. When  $R$  is very large, it approximates to

$$\lambda = 64a/R_c^n R^{1-n} = 0.339/R^{0.265}$$

on inserting Menneret's values for  $a$  and  $n$  and on putting  $R_c = 2,000$ . The well-known formula of Blasius (1912) for large  $R$  is

$$\lambda = 0.316/R^{0.25}$$

That of Nikuradse is

$$\lambda = 0.0032 + 0.221/R^{0.237}$$

A more general formula, with a theoretical basis, is that verified by Nikuradse<sup>2</sup>:

$$\lambda^{-1} = 2 \log (R\lambda^3) - 0.8$$

When the pipe is rough, we can approximately take the roughness into account by adding the tautometric product  $S \equiv e/r$ , where  $e$  is the height of a protuberance, so that

$$\lambda = \phi(R, S)$$

Fig. 3 (III) (taken from Bakhmeteff, p. 35) illustrates Nikuradse's experiments on artificially prepared sand surfaces with  $S$  varying from 1/507 to 1/15. The straight line I corresponds to Poiseuille's formula, while II is the Blasius line for a smooth pipe. For sufficiently large  $R$  all the curves become  $\lambda = \text{constant}$ , depending only on the roughness. These hydraulic experiments are an excellent illustration of the importance of tautometric products in grouping and classifying experimental results.

We may add a few remarks on the 'drop method' for measuring surface-tension (discussed on p. 515). The best method for correcting Tate's so-called law is that given by W. Harkins and F. Brown.<sup>3</sup> We have two tautometric products:

$$\begin{aligned} \text{weight}/(\text{s. tension} \times \text{radius of tube}) &= mg/rs \\ \text{radius}/\text{cube root of volume} &= r/v^{\frac{1}{3}} \equiv R \end{aligned}$$

<sup>1</sup> Menneret, *Mouvement oscillatoire et mouvement uniforme des liquides dans les tubes cylindriques*, Grenoble, 1911.

<sup>2</sup> See the graph in Bakhmeteff, *The Mechanics of Turbulent Flow*, Princeton, 1936, p. 84.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1919, **41**, 499.



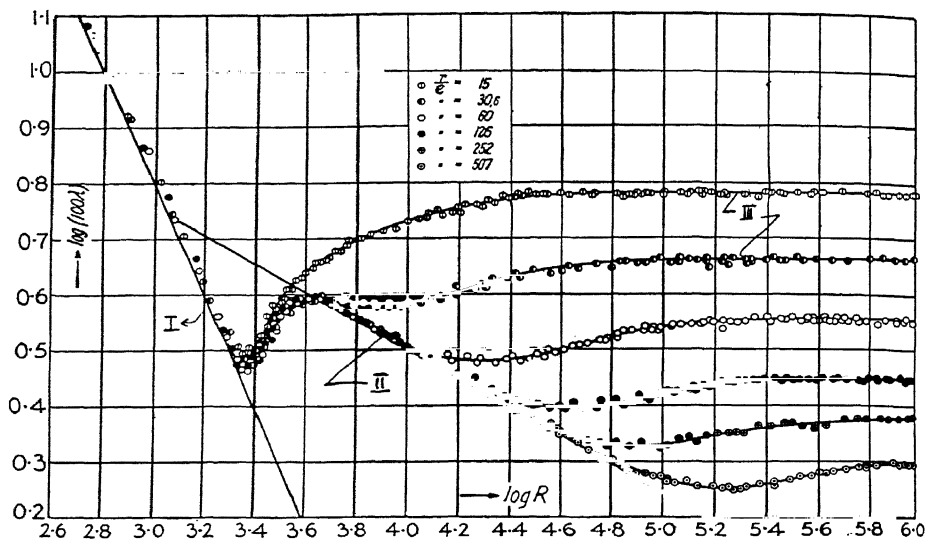


FIG. 3 (III)

Hence we can take

$$mg = 2\pi rs \phi(R)$$

The variation of  $\phi(R)$  with  $R$  is shown in Fig. 4 (III).

The results for various liquids and for tubes of glass or brass all fall upon the curve. Inasmuch as the experimental values of  $\phi$  vary from 0.5987 to 0.924, Tate's law ( $\phi = \text{constant}$ ) is incorrect.

Rayleigh's formula given on p. 510 also illustrates the principle of tauto-metric products. We have by obvious general considerations

$$f(s, \rho, g, r, h) = 0$$

where  $s$  is the surface-tension and  $\rho$  the density of the liquid, and  $h$  is the

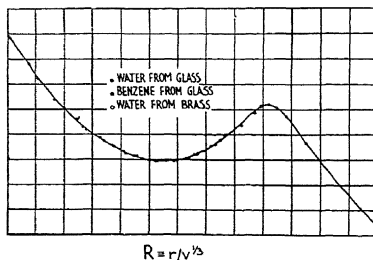


FIG. 4 (III)

capillary rise at the midpoint of the tube (radius  $r$ ). There are two tauto-metric products:  $s/g\rho r^2$  and  $x \equiv h/r$ . Hence

$$s/g\rho r^2 = \phi(x)$$

According to Poisson and Rayleigh

$$\phi(x) = x + 1/3 - 0.1288/x + 0.1312/x^2 + \dots$$

Except near the critical point  $x$  is large, so that the last two terms are negligible.

In the above examples at least two tautometric products were involved. We have not thought it necessary to illustrate the simpler case in which only one such product occurs. Two examples of the latter may be given in conclusion. Assuming that the period of a simple pendulum depends only on its length and on gravity, the only tautometric product is  $tg^{\frac{1}{2}}l^{-\frac{1}{2}}$ , as may be seen by putting

$$T = G^x L^y = (LT^{-2})^x L^y$$

Equating indices, we have  $x = -\frac{1}{2}$ ,  $y = +\frac{1}{2}$ . Hence  $t = C(l/g)^{\frac{1}{2}}$ . *Aliunde* we know that  $C = 2\pi$ .

Again, suppose that the vibration-frequency ( $n$ ) of a musical string depends only on its length ( $l$ ), its mass ( $m$ ) and its tension ( $f$ ). The tautometric product of these four quantities is obtained by putting

$$T^{-1} = N = L^x M^y (MLT^{-2})^z$$

Equating indices, we have  $x = -\frac{1}{2}$ ,  $y = -\frac{1}{2}$ ,  $z = \frac{1}{2}$ . Hence

$$n = C(f/ml)^{\frac{1}{2}}.$$

### SECTION 3: ELECTRICAL UNITS<sup>1</sup>

Consideration of magnetic and electrical units has become almost a bugbear to students—and perhaps to their teachers—owing to the enormous mass of meaningless ‘dimensions’ which clutters up most textbooks. We do not propose to argue here against current misconceptions. We shall merely give a brief constructive exposition quite sufficient for any working physicist or chemist. Our treatment is quite elementary and is based on the simple idea of measure-ratio already explained. The subject will be still further simplified if at the outset we bear certain points in mind.

(1) The initial law on which magnetic theory is built may be taken to be the formula for the force between poles:  $f = mm'/\beta r^2$ , where  $\beta$  is the magnetic constant. It is a waste of time to consider different values of  $\beta$ ; it is the universal practice to take  $\beta = 1$ . That is, there is only *one* system of magnetic units.

(2) Magnetic permeability ( $\mu$ ) and electrical inductivity or dielectric constant ( $\kappa$ ) are, by their very definition, tautometric. Their measure-ratio is always unity; in current jargon, they are ‘dimensionless’. This is universally admitted in practice; but this elementary fact has become obfuscated by meaningless controversies.

(3) The C.G.S. system is universally employed in magnetic and electrical measurements. Hence it is a sheer perversion of energy to investigate what our measures would become if we were to adopt a different—e.g. the British engineering—system. In other words, whatever different electrical measures we adopt, we always take the measure-ratios of length, mass and time to be unity, i.e.  $L = M = T = 1$ . Thus, at one swoop, the ‘dimensions’ of electrical textbooks are exploded.

The fundamental formula of electricity is Coulomb’s law of force between point-charges:  $f = qq'/\alpha r^2$ , where  $\alpha$  is the electrical constant. There are two systems of units. In the electrostatic, which we shall call *elst*,  $\alpha = 1$ ; in the electromagnetic, which we shall call *elm*,  $\alpha = 1/c^2$ , where  $c$  is a quantity that can be determined experimentally and is found to be  $3 \times 10^{10}$  (numerically the velocity of light). Let us denote *elst* measure by the subscript 1 and *elm* measure by the subscript 2, so that  $\alpha_1 = 1$  and  $\alpha_2 = c^{-2}$ . The force between the same pair of point-charges, measured in *elst* and then in *elm* measure, is

$$q_1 q_1' / \alpha_1 r^2 = f = q_2 q_2' / \alpha_2 r^2$$

so that

$$q_1 / q_2 = q_1' / q_2' = \alpha_1^{\frac{1}{2}} / \alpha_2^{\frac{1}{2}} = c$$

<sup>1</sup> A fuller discussion will be found in my *Electromagnetics* (London, Longmans, 1938).

Or, in our previous notation,

$$Q = [\alpha^4] = c$$

Perhaps it is as well to emphasize once more, in view of current mystifications, that there is no esoteric significance whatever in our use of capital letters or of square brackets. It is merely a convenient shorthand notation applied to elementary algebra.

This simple assumption suffices to give us the complete scheme connecting elst and elm measures. This is exhibited in the following table, wherein for convenience we deviate from the usual notation (e.g.  $\rho$  for resistance):

Quantity	Symbol	Equation	<u>Elst measure</u> <u>Elm measure</u>
Charge	$q$		$Q = c$
Current	$j$	$q = jt$	$J = c$
Electric intensity	$E$	$Ej = \text{force}$	$[E] = 1/c$
E.M.F.	$V$	$Vq = \text{work}$	$[V] = 1/c$
Capacity	$C$	$C = q/V$	$[C] = c^2$
Resistance	$\rho$	$V = j\rho$	$R = 1/c^2$

This is all we require to know. For example, if the elst measure of capacity is  $C_1$ , the elm measure is given by  $C_1/C_2 = c^2$ , i.e.  $C_2 = c^{-2}C_1$ .

Let us next consider one of the electromagnetic laws, say the expression for the magnetic intensity at the centre of a circular current

$$H = 2\pi j/ar$$

where  $a$  is a constant which is taken as unity when the current ( $j$ ) is measured in elms. It follows that  $a = c$  when the current is measured in elsts, for  $j_1/j_2 = q_1/q_2 = c$ . We have

$$2\pi j_2/r = H = 2\pi j_1/cr$$

That is, the same  $H$ —measured, for example, against the earth's magnetic field on a tangent galvanometer—is given by either expression. The measure of  $H$  has nothing to do with our change of electrical measurement, no more than has the measure of mechanical force. Accordingly we can tabulate our measure-systems as follows:

$$\begin{aligned} \text{Mag measure: } \beta &= 1 \\ \text{Elst measure: } \alpha_1 &= 1, \alpha_1 = c \\ \text{Elm measure: } \alpha_2 &= 1/c^2, \alpha_2 = 1 \end{aligned}$$

The 'practical' measures are certain multiples of the elm measures of current and resistance; namely, denoting pra-measure by letters without subscripts,

$$\begin{aligned} J &= j_2/j = 10^{-1} \\ R &= \rho_2/\rho = 10^9 \end{aligned}$$

Thus we have:

Quantity	Pra unit	Equation	<u>Elm measure</u> <u>Pra measure</u>
Current	Ampere		$J = 10^{-1}$
Resistance	Ohm		$R = 10^9$
Charge	Coulomb	$q = jt$	$Q = J = 10^{-1}$
E.M.F.	Volt	$V = j\rho$	$[V] = JR = 10^8$
Capacity	Farad	$C = q/v$	$[C] = R^{-1} = 10^{-9}$

For example, if a capacity is  $C_1$  elsts,  $C_2$  elms, and  $C$  farads,

$$C_2/C = 10^{-9}$$

Hence

$$c^{-2}C_1 = C_2 = 10^{-9}C$$

At the Chicago Congress of 1893 and at a subsequent London Conference the ohm and the ampere were defined with reference to certain laboratory specifications. This resulted in *slightly* different values of  $R$  and  $J$  from  $10^9$  and  $10^{-1}$  respectively. These discrepancies are of relevance only in extremely accurate work; and in any case the General Conference of Weights and Measures has decided, with the approval of thirty-two countries, to revert to the absolute values ( $J = 10^{-1}$ ,  $R = 10^9$ ) at the beginning of 1940. (Of course, there remain the important practical problems of calibrating national standards and commercially reproducible instruments; with these we are not here concerned.)

To obtain the pra-system, as described so far, we start with certain *selected* equations in elm measure and we then change the measures of current and resistance in the respective ratios  $J = 10^{-1}$  and  $R = 10^9$ . That is, the measure-ratios of  $V$  and  $C$  are so chosen as to leave the form of the equations  $V = jQ$  and  $C = q/V$  unaltered. There are a number of other pra-measures introduced, sometimes in a rather haphazard fashion, which are designed to absorb any multiplier (power of 10) which may occur in various other equations. Let us enumerate these, using the suffix 2 to denote elm measures and using letters without suffix to denote pra measures.

(1) The equation

$$V_2 q_2 = w \text{ (work in ergs)}$$

becomes

$$[VQ]Vq = w, \text{ or } Vq = 10^{-7}w$$

We can eliminate the factor  $10^{-7}$  by measuring work in joules (joule =  $10^7$  ergs) so that the new measure is  $w' = 10^{-7}w$ . Thus the equation becomes

$$Vq = w'$$

which is literally identical with the elm equation from which we started.

(2) Similarly the elm equation for induced E.M.F. (where  $L$  is the self-induction)

$$V_2 = -L dj_2/dt$$

becomes

$$[V]V = -LJdj/dt$$

or

$$V = -10^{-9}Ldj/dt = -L'dj/dt$$

where  $L' = 10^{-9}L$  is called the pra-measure (in henries) and is introduced merely in order to eliminate the numerical factor.<sup>1</sup>

(3) The elm-mag equation

$$V_2 = -dN/dt$$

<sup>1</sup> Observe that we did not use the symbol  $L_2$  to denote the elm measure of self-induction, for there is no such measure.  $L$  depends only on the geometrical configuration (length-measure in centimetres) and is neither elm nor elst.

where  $N$  is magnetic flux, becomes

$$[V]V = -dN/dt$$

or

$$V = -10^{-8}dN/dt = -dN'/dt$$

where  $V$  is in pra-units (volts),  $N$  is in mag units (maxwells) and  $N' = 10^{-8}N$  is the measure in terms of the weber or pra-maxwell ( $= 10^8$  maxwell).

(4) The equation  $H = 2\pi j_2/r$ , where  $H$  is in mag measure (oersteds) and  $j_2$  is in elm measure, becomes

$$H = 2\pi Jj/r = 2\pi j/10r$$

or

$$2\pi j/r = 10H = H'$$

where  $j$  is in amperes and  $H' = 10H$  is measured in terms of the pra-oersted ( $= 10^{-1}$  oersted).

(5) On the other hand, in the expression for flux

$$N = \int B_n dS$$

$N'/N$  is as in no. (3) taken to be  $10^{-8}$ . So to eliminate the  $10^{-8}$ ,  $B'/B$  is also taken as  $10^{-8}$ , giving

$$N' = \int B_n' dS$$

$B'$  is then said to be measured in terms of the pra-gauss ( $= 10^8$  mag units).<sup>1</sup>

We can now add the following supplementary table:

Quantity	C.G.S. unit	Pra unit	<u>C.G.S. measure</u>
Energy	Erg	Joule	<u>Pra measure</u> $10^7$
Inductance		Henry	$10^9$
Quantity	Mag. unit	Pra unit	<u>Mag measure</u>
Magnetic flux	Maxwell	Pra-maxwell (weber)	<u>Pra measure</u> $10^8$
Mag. intensity	Oersted	Pra-oersted	$10^{-1}$
Mag. induction	Gauss	Pra-gauss	$10^8$

Various attempts have been made to produce consistency among these pra-measures; but they have all failed, even the latest (Giorgi's). They must be regarded as mere empirical dodges for suppressing powers of 10 in various formulae.

<sup>1</sup> Observe that this unit is here called gauss, though in dealing with  $H$  it was just called oersted.

## SECTION 4: DYNAMICAL SIMILARITY

In the transformation  $l_1 = Ll_2$ ,  $m_1 = Mm_2$ ,  $t_1 = Tt_2$ , we interpreted  $l_1$  and  $l_2$ , &c., to mean two measures of the same magnitude in different units. We shall now show that this transformation is susceptible of another very useful interpretation. Instead of comparing two sets of measurements of the same system referred to different units, let us compare the measurements of two different systems referred to the same units. We shall call the systems  $S_1$  and  $S_2$  and we assume a one-to-one correspondence between them so that for every quantity  $q_1$  in  $S_1$  there exists a corresponding conspecific quantity  $q_2$  in  $S_2$ . Capital letters, such as  $Q = q_1/q_2$ , will now denote the ratios of corresponding measures. Thus to every length  $l_1$ ,

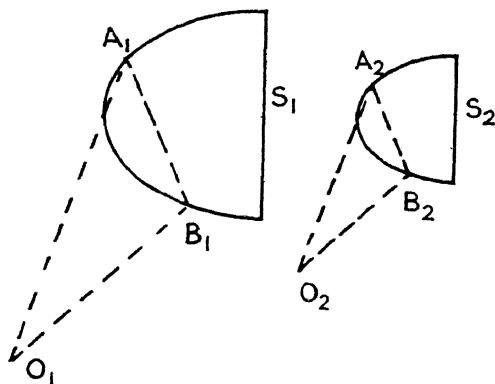


FIG. 5 (III)

$l_1' \dots$  in  $S_1$ , there corresponds a length  $l_2 = Ll_1$ ,  $l_2' = Ll_1' \dots$  in  $S_2$ . Formerly  $L$  was the same for the measure-pairs of any Length; that is, no matter what Length we chose for measurement relatively to the two given units,  $L$  was the same, being in fact the inverse ratio of these two units. So now we take  $L$  to be the same for all corresponding length-pairs in the two given systems (measured in the same arbitrary unit); that is, no matter which pair of corre-

sponding lengths we choose for comparison, their ratio is the *constant*  $L$ . Similarly we assume  $M$  and  $T$  to be constant. Two mechanical systems so related are said to be *dynamically similar*.

Let us analyse these conditions.  $L = \text{constant}$ , implies geometrical similarity. If the lettered points (Fig. 5 (III)) designate corresponding points, we have

$$O_1A_1/O_2A_2 = O_1B_1/O_2B_2 = A_1B_1/A_2B_2 = \&c. = L$$

The two systems represent geometrically the same figure on different scales, like two differently sized maps of the same region.

If both  $L$  and  $T$  are constant, we have what may be called kinematic similarity. Suppose that the systems are geometrically similar at the instant  $t_1 = t_2 = 0$ , and that elements in  $S_1$  are moving relatively to  $O_1$  and elements in  $S_2$  relatively to  $O_2$ . Then the configuration which  $S_1$  has after the lapse of any interval  $t_1$  is similar to that which  $S_2$  has after the

lapse of an interval  $t_2 = t_1/T$ , where  $T$  is a constant. The measure-ratio of velocity—that is, the ratio of the velocities of corresponding elements at corresponding moments—is

$$V = \frac{v_1}{v_2} = \frac{dl_1/dt_1}{dl_2/dt_2} = \frac{dl_1}{dl_2} \frac{dt_1}{dt_2} = \frac{L}{T}$$

It is therefore constant. Similarly the measure-ratio of acceleration is the constant  $L/T^2$ .

If the three ratios  $L$ ,  $M$ ,  $T$  are constant, we have dynamical similarity. That is, in addition to the foregoing conditions, we have

$$m_1/m_2 = m_1'/m_2' = \&c. = M$$

Then clearly the corresponding forces are in the constant ratio  $F = ML/T^2$ . And in general all our previously tabulated logometric formulae hold with this new interpretation. Formerly we took the measure-ratio of a quantity to be the factor ( $Q$ ) by which its measure ( $q_2$ ) in one set of units must be multiplied to give its measure ( $q_1$ ) in another set of units. We now take measure-ratio to be the factor ( $Q$ ) by which the measure ( $q_2$ ) of a quantity must be multiplied in order to give the measure ( $q_1$ )—in the same units—of the corresponding quantity in a dynamically similar system. All formulae of the type  $Q = L^a M^b T^c$  are still valid.

This notation provides us with a succinct method of dealing with similar systems, and in particular with a body and its model. Let us take two simple examples.

(1) Suppose that the only forces occurring are elastic. If  $q$  is the modulus concerned,  $q$  = stress/strain. The measure-ratio of strain is obviously unity. Hence

$$Q = F/L^2 = M/LT^2$$

The velocity ( $v$ ) of an elastic wave depends on  $q$  and the density. Since  $V = L/T$  and the measure-ratio of density is  $D = M/L^3$ , we have

$$V = Q^{1/2} D^{-1/3}, \text{ or } v = \text{const. } (q/\rho)^{1/2}$$

For similar systems—e.g. bells or tuning-forks—made of uniform isotropic material and vibrating in virtue of elasticity, the frequency ( $n$ ) depends on the linear dimensions ( $l$ ) and on  $q$  and  $\rho$ . Since  $N = 1/T$ , we have

$$n = \text{constant } q^{1/2} \rho^{1/3} l^{-1}$$

Hence for similar vibrators of the same material, the pitch varies inversely as the linear dimensions. This law was stated by Savart in 1825 as the result of elaborate experiments.

(2) Suppose that the only forces involved are those due to gravity. Since  $g$  is the same for both,

$$I = G = L/T^2 = V^2/L$$

Hence the periods of similar pendulums vary as the square root of the lengths. If in addition there are forces proportional to area  $\times$  speed<sup>2</sup>, as is approximately true for ship resistance,

$$F = V^2 L^2 = L^3 = M = W$$

if the density is the same so that  $M = L^3$ . Thus the resistance-forces are in the same ratio as the gravity-forces (weights), and the systems remain



dynamically similar. The rule  $V^2 = L$  is known as Froude's law : corresponding velocities (in a ship and its model) vary as the square root of the scale.

The differential importance of various types of forces, i.e. their relative intensities as the geometrical scale varies, is of great significance in chemistry, physics, and biology.<sup>1</sup> Compare, for instance, weight and elastic forces. We have

$$F_1/F_2 = DL^3/QL^2 = LD/Q$$

Hence for two systems of the same material ( $D = Q = 1$ ), gravity-forces increase faster than elastic forces as the scale is increased. Since there is an elastic limit, the larger structure tends to be crushed by its own weight. Thus of two geometrically similar bridges, the larger is the weaker. (Since the human thigh-bone breaks under about ten times the human weight per unit surface, a giant 60 feet high could not stand.) In nature geometrical similarity does not hold ; an elephant is built on a different plan from that of a gazelle, so that the required elastic forces may be available for the greater weight.

Compare gravity and the force of surface-tension :

$$F_3/F_1 = SL/DL^3 = S/DL^2$$

Thus as we reduce the scale ( $L < 1$ ), surface-tension becomes more important, e.g. for an insect.

Compare viscous and elastic forces :

$$F_2/F_4 = QL^2/EVL = QL/EV$$

where E stands for  $\mu_1/\mu_2$ . Hence it is clear that the higher the speed, the more important is compressibility and the less important is viscosity.

These elementary considerations bring out the important point that geometrical or kinematic change of scale in a phenomenon may involve considerable dynamical alteration. We generally express this by some such phrase as 'neglecting viscosity'. Interpreted literally, the statement that such-and-such a force or quantity is negligible, has no meaning ; for a measure can be varied arbitrarily by changing units. What is meant is that, say, a certain type of force is, in the given case, negligible relatively to some other type of force.

In connection with changes of units we applied the term *tautometric* to those quantities or products whose measure is unaffected by a change of units. We shall now apply the term *symmetric* to those quantities or products which have the same value (in any one set of units) in two similar systems. The terms are not always synonymous. So-called 'dimensional constants', such as the gravitational constant ( $\gamma$ ) and the speed of light in vacuum ( $c$ ) are not tautometric ; but they are symmetric, for

$$[\gamma] = \gamma_1/\gamma_2 = 1$$

since the constant is the same in all systems. On the other hand,  $\kappa$  and  $\mu$ , though necessarily tautometric, need not be symmetric ; for  $[\kappa] = \kappa_1/\kappa_2$  and the inductivities in the two systems need not be equal.

We can now apply our new interpretation to the general equation (2).

<sup>1</sup> Cf. J. B. S. Haldane, 'On Being the Right Size', in *Possible Worlds and Other Essays*, 1927, pp. 18-26.

That is, the equation holds for all similar systems, and the  $p$ 's denote symmetric products. We must notice that, while there are certain derived quantities (such as velocity) which are determined by the basic ratios ( $L, M, T$ ), there are others which are not determined by  $L, M, T$  but rather serve to determine these ratios. Such quantities, which are dependent on external agencies or on complex constitutional factors, may be called the *characteristics* of the system. Consider the hydrodynamical equation already investigated :

$$\phi(f/\rho v^2 l^2, \mu/\rho \nu l) = 0$$

Here we have two characteristics  $\rho$  and  $\mu$ , whose measure-ratios are  $D = M/L^3$  and  $E \equiv [\mu] = M/LT$ . Now the ratios of density and viscosity are not in the least influenced or determined by the  $L, M, T$  that we choose. Leaving temperature out of account, we can say that they are determined by the liquids we select for our systems; for two given liquids  $D$  and  $E$  are fixed, and we must adjust our  $L, M, T$  accordingly. That is, our choice is limited by having to satisfy the relations:  $M = DL^3$ ,  $T = L^2 D/E$ , so that while  $L$  is arbitrary  $M$  and  $T$  are determined for any selected scale-ratio. If the phenomenon also depends on gravity ( $g$ )—e.g. wave-making by a surface-body—we have three characteristics  $g, \mu, \rho$ ; and we have to include a third symmetric product  $gl/v^2$  in the arguments of the function  $\phi$ . Since  $G = L/T^2$  (and in practice is unity), the ratios  $L, M, T$  are now uniquely determined :

$$L^3 = E^2/GD^2, \quad M = E^2/GD, \quad T^3 = E/G^2D$$

Thus for any one system with given  $g, \mu, \rho$ , there is only one other dynamically similar system.

Using  $g, \mu, \rho$  as probasic quantities, we can express the equation in the form

$$F\left(\frac{f}{u^2/\rho}, \frac{v}{(g\mu/\rho)^{\frac{1}{3}}}, \frac{l}{(\mu^2/g\rho^2)^{\frac{1}{3}}}\right) = 0$$

or as

$$F(\alpha f/f_0, \beta v/v_0, \gamma l/l_0) = 0$$

where  $f_0, v_0, l_0$  are particular values given by

$$f_0 = \alpha \mu^2/\rho, \quad v_0 = \beta (g\mu/\rho)^{\frac{1}{3}}, \quad l_0 = \gamma (\mu^2/g\rho^2)^{\frac{1}{3}}$$

and  $\alpha, \beta, \gamma$  are arbitrary constants. If we choose these constants to satisfy  $F(\alpha, \beta, \gamma) = 0$ , then  $f = f_0, v = v_0, l = l_0$ , form one possible set of values. From this we can deduce a relation

$$\psi(f/f_0, v/v_0, l/l_0) = 0$$

This development is given here, not for any intrinsic interest, but as an analogy introductory to an equation which we shall meet in Section 6.

## SECTION 5: HEAT TRANSMISSION

There have been interminable discussions concerning the 'dimensions' of temperature, heat, and specific heat. They are a waste of time; in any case they are irrelevant for our purpose, as we have not employed 'dimensions'—whatever they are supposed to mean. Temperature may be, and usually is, measured surrogatively by a length, i.e. the height of a thermometric column. But this no more implies that temperature *is* length than the reading of a clock implies that time is an angle. The length involved is not one of the spatial dimensions of the system, it is an independent variable; just as the motion of the clock-hand is not the motion of one of the elements of the system. The definition of heat is given by

$$q = ms\theta$$

where  $m$  is the mass of the body heated through a temperature-interval  $\theta$ . The factor  $s$ —specific heat or thermal capacitance—is arbitrary in absolute value; so we take  $s$  for water as unity—if we are concerned with refined measurement, we can say: at a specified temperature. Then the quantity of heat necessary to raise an equal mass of water through the same temperature-interval is given by:  $q_0 = m\theta$ . That is, specific heat is tautometric:  $s = q/q_0$ . Of course, it does not follow that it is symmetric; for we may be concerned with two bodies having two different specific heats.

We defined *dynamically* similar systems by the constancy of the ratios  $L, M, T$ . If to these we add the temperature-ratio  $\Theta$ , we can define *physically* similar systems as those for which  $L, M, T, \Theta$  are constant (basic ratios). The general formula for measure-ratio will then be

$$Q = L^x M^y T^z \Theta^w$$

We shall now consider briefly some physically similar systems, first dealing with natural convection. It is to be understood that we are not investigating experimental details and technical complications. Our object is merely to illustrate general principles and to give the reader a correct orientation free from unnecessary extra-scientific ideas. The following new quantities are involved:

Quantity	Symbol	Measure-ratio
Temperature-excess of body		$\Theta$
Heat-loss per unit area per unit time per		
	$h$	$H = Q/L^2 T \Theta$
Thermal conductivity of fluid <sup>1</sup>	$k$	$K = Q/LT\Theta$
Specific heat of fluid per unit volume	$c = sq$	$C = Q/L^3 \Theta$
Thermal coefficient of expansion of fluid	$\alpha = -\frac{1}{q} \frac{dq}{d\theta}$	$A = 1/\Theta$

In assigning the measure-ratios it will be observed that we have left  $Q$

<sup>1</sup> This is defined by:  $dq/dt = k \times \text{area} \times d\theta/dx$ .

as the symbol for heat-ratio. The reason is simple. Heat may, in principle, be supposed to be measured by the temperature-rise in *any* body in accordance with the equation  $q = ms\theta$ . If we suppose it is measured by means of the fluid here concerned, we have

$$q = ms\theta = vc\theta$$

so that

$$Q = L^3C\Theta$$

But this equation occurs already in the logometric formula for C. It makes no difference whatever to substitute  $Q = L^3C\Theta$  in the expressions for H and K and to omit the formula for C. We can thus eliminate Q completely if we so wish; and if Q is retained in the measure-ratios, it must be regarded as standing for  $L^3C\Theta$ .

It is, however, worth while to observe that these logometric formulae can also be interpreted as referring to a change of units. (In fact, it is necessary that this should be so, for we are going to apply the general formula (2), which was proved on the assumption that the  $p$ 's were tautometric products.) We have said above that  $s$  (specific heat per unit mass) is tautometric. But this is true only in virtue of the logically subsequent convention that the specific heat of water is to be taken as unity. There is nothing obligatory or apodictic in this convention; and if we wish to make the most general change of units, we must ignore it. The fact that in practice we do not make such a change—we never make  $s = 3.5$  for water—is irrelevant when our object is to find the most general form of the tautometric products involved in a general thermal equation. In practical questions of units we put  $S = 1$  and take  $Q = M\Theta$ . For example, suppose we wish to find the relation between the British Thermal Unit and the gram-calorie. We have, as in formula (1),

$$\text{B.T.U.} \times (\text{mass of 1 lb.}) \times \text{Fahr.} = \text{cal.} \times \text{gm.} \times \text{Cent.}$$

That is,

$$\frac{\text{B.T.U.}}{\text{cal.}} \cdot \frac{\text{gram}}{\text{mass of 1 lb.}} \cdot \frac{\text{Cent.}}{\text{Fahr.}} = 453.6 \times \frac{5}{9} \\ = 252$$

Underlying this is the convenient (but not necessary) convention that specific heats are to remain unchanged. If we do not make this assumption, we have

$$Q = MS\Theta = L^3C\Theta$$

This gives us the measure-ratio of heat consequent on changes in the measures of length, mass, heat-capacity, and temperature. In other words, the logometric formulae we have given are equally capable of being interpreted as referring to a change of units. And the products we shall presently employ can be regarded either as tautometric or as symmetric. Though the latter interpretation is more useful, the former is required in order to justify our use of the general theorem (2).

We shall now assume that  $h$  depends on the following quantities:  $\theta, c, k, d, \mu/\rho, ga$ . Here  $d$  is a linear dimension; in the case of a long cylinder we take  $d$  to be the diameter and we regard the length as irrelevant. In taking  $\mu$  and  $\rho$  to occur in the form  $\mu/\rho$  (measure-ratio  $L^2/T$ ), just as

when we take the volume-capacity  $c$  instead of the mass-capacity  $s$ , we are eliminating  $M$  as one of the basic ratios involved. We assume that  $g$  and  $\alpha$  occur only in the combination  $ga$ , i.e. we take the change in density to be negligible except in so far as it alters the weight of unit volume. We take  $\mu$  and  $k$  to be constant, i.e. to have their average values for the range of temperature involved. It is now <sup>1</sup> easy to see that we have three symmetric products :

$$S \equiv hd/k$$

$$P \equiv gac^2d^3\theta/k^2$$

$$Q \equiv c\mu/k\rho$$

Hence we have

$$S = f(P, Q)$$

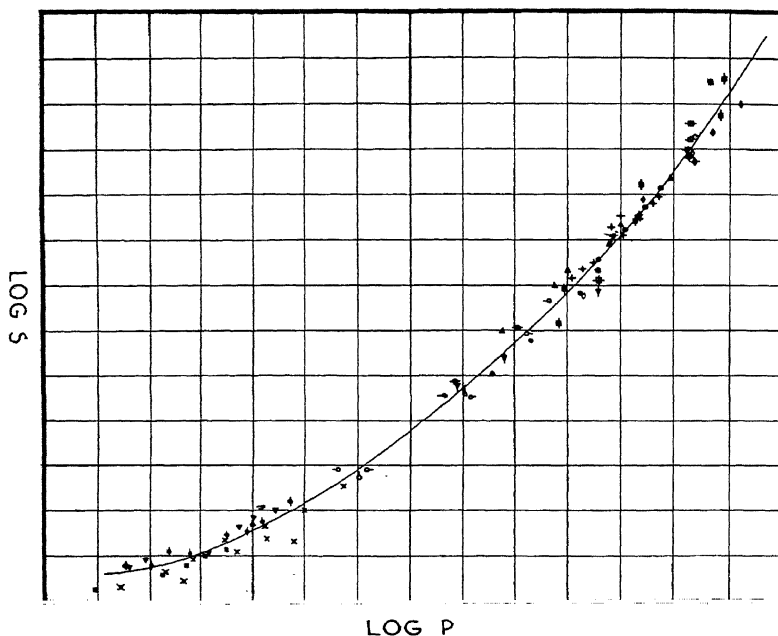


FIG. 6 (III)

For diatomic gases we can take  $Q$  to be constant (0.74). Fig. 6 (III) represents <sup>2</sup> the results of various observers on the natural convection from a horizontal cylinder in air or other gas.  $\log S$  is plotted against  $\log P$ . It will be noticed that the points lie on the same curve, though the cylinders varied in diameter from fine wires to 10-inch pipes, the temperature-

<sup>1</sup> These are often called after certain physicists:  $S$ , Nusselt;  $Q$ , Prandtl;  $R$ , Reynolds;  $P/Q^2$ , Grashof.

<sup>2</sup> M. Fishenden and O. Saunders, *The Calculation of Convection Heat Transmission*, 1932, p. 96.

## HEAT TRANSMISSION

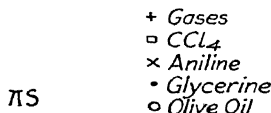
differences ranged from 2,000° to 500° Fahr., and the gases were air, carbon dioxide, and hydrogen at different pressures.

Since the steady stream-velocity is determined by a balance between gravity and the retarding viscous force, it is natural to expect that  $g$  and  $\mu/\rho$  occur only in the combination  $g\rho/\mu$ . This is equivalent to assuming that P and Q occur only in the form

$$P/Q = g\rho acd^3\theta/k\mu$$

For the heat transfer between a single horizontal cylinder and a fluid (in natural convection) Nusselt <sup>1</sup> gave the formula

$$S = C(P/Q)^{\frac{1}{4}}$$



P/Q

FIG. 7 (III)

where C is about 0.5. This gives the widely verified result:  $h$  varies as  $\theta^{\frac{1}{4}}$ , which also holds approximately for vertical plates in air.

A. H. Davis measured the heat-loss from wires of diameters 0.0083 and 0.0155 cm. in air, toluene ( $Q = 7.24$ ), carbon tetrachloride, aniline, olive oil, and glycerine ( $Q = 7940$ ). Fig. 7 (III) shows  $\pi S$  plotted against  $P/Q$ . The points fall on a single curve.<sup>2</sup>

Let us now turn to forced convection, i.e. the cooling or the heating of a wire or pipe in a stream of fluid. This case is of practical importance, e.g. for radiators and air-cooled engines. If we assume that the gravity current is negligible, the argument  $ga$  does not occur. But we have now to

<sup>1</sup> Rice, *Int. Crit. Tables*, 1929, 5, 234. See the curve of  $\log S$  against  $\log (P/Q)$  in McAdams, *Heat Transmission*, 1933, p. 248.

<sup>2</sup> A. H. Davis, *Phil. Mag.*, 1922, 4, 938. The heat loss per unit length per unit time per degree excess is  $\pi h d = \pi k S$ . The upward extension of the curve is based on other results for gases.

take account of  $v$ , the relative velocity of the body and the fluid, e.g. the velocity of the stream past the immersed body or the mean speed at the section of the pipe. We have three symmetric products:

$$S \equiv hd/k, \quad Q \equiv c\mu/kq, \quad R \equiv qvd/\mu$$

The equation is <sup>1</sup>

$$S = \phi(Q, R)$$

In the case of heat transfer by forced convection between the external surface of a circular cylinder and a stream of air or other fluid flowing perpendicularly to the axis of the cylinder, Ulsamer <sup>2</sup> proposed the formula

$$S = AQ^m R^n$$

where for  $R$  between 50 and 10,000:  $A = 0.60$ ,  $m = 0.31$ ,  $n = 0.50$ .

For heat transfer in the case of a fluid in turbulent flow inside a clean circular pipe, Dittus and Boelter <sup>3</sup> have given the formula

$$S = AQ^m R^n$$

where  $A = 0.0225$ ,  $m = 0.4$ ,  $n = 0.8$ . (When the fluid is being *cooled*, we must take  $m = 0.3$ .) This has been successfully checked on many fluids—air and other gases, water, hydrocarbon oils, various organic fluids—with  $Q$  ranging from 0.73 to 95 and  $R$  varying between 2,500 and 160,000.

These results on heat-transmission have not only an interest of their own as well as practical applications. They also aptly illustrate the importance and convenience of expressing experimental data in the form of tautomeric (or symmetric) products. And they show how far, without making any appeal to physical theory, we can synthesize and co-ordinate results merely by utilizing general metrical considerations.

<sup>1</sup> Rayleigh, *Nature*, 1915, 95, 66.

<sup>2</sup> *Forschung*, 1932, 3, 4. It is not so accurate for  $R$  between 0.1 to 50 ( $A = 0.91$ ,  $m = 0.31$ ,  $n = 0.385$ ). Small proposed the formula:  $A = 2.96$ ,  $m = n = 0.626$ .—*Phil. Mag.*, 1935, 19, 252. Since  $QR = cvd/k$ , this means that the density is eliminated.

<sup>3</sup> *Univ. Calif. Pub. in Eng.*, 1930, 2, 443. The equation holds for hydrocarbon oils only when  $R > 7,000$ ; for lesser values of  $R$  the curve of Morris and Whitman must be used.—*Ind. Eng. Chem.*, 1928, 20, 238; or better, e.g. in Badger and McCabe, *Chemical Engineering*, 1936<sup>2</sup>, p. 135.

## SECTION 6: MOLECULAR SIMILARITY

We shall now attempt to give a synthetic presentation of a number of formulae in physico-chemistry. The following notation will be employed :

$m$  = mass of a single gas-molecule

$m_H$  = mass of a hydrogen *atom* =  $1.665 \times 10^{-24}$  gram

$w$  = molecular weight =  $m/m_H$  (e.g.  $w = 2$  for  $H_2$ )

= mass of one mol of the gas

$n$  = no. of molecules in one mol =  $w/m = 1/m_H$

$v$  = molal volume =  $w/\rho$

$v_m$  = 'molecular volume' =  $m/\rho = vm_H$

$\theta$  = absolute temperature

$j$  = mechanical equivalent of heat

=  $4.184 \times 10^7$  erg/cal.

According to the elementary theory of a perfect gas:  $p = \frac{1}{3}\rho u^2$ ,  $\frac{1}{2}mu^2 = g\theta$ , where  $g$  is a constant. Hence for a mol

$$pv = r\theta, \text{ where } r = 2g/3m_H$$

It is found that  $r = 8.313 \times 10^7$  erg/grad. Hence

$$r/j = 1.987$$

$$g = 2.008 \times 10^{-16}$$

$$g/jm_H = 2.882$$

Instead of  $g$  we may of course use Boltzmann's constant

$$k = rm_H = 1.372 \times 10^{-16}$$

We shall now proceed to a further approximation. Consider two statistically similar masses of gas, each being one mol and therefore containing  $n = 1/m_H$  spherical<sup>1</sup> molecules. As probasic quantities we take :

(1)  $m$  the mass of a molecule or  $w$  the total mass

(2)  $v/n$  the molecular volume or  $v$  the total volume

(3)  $g\theta$  or  $r\theta$

We then have

$$L = V^{\frac{1}{3}}, M = W, T = W^{\frac{1}{3}}V^{\frac{1}{3}}(R\theta)^{-\frac{1}{3}}$$

Though  $g$ ,  $r$  and  $j$  are constants, i.e. symmetric but not tautometric, so that their measure-ratios for similar systems are unity, we shall use the symbols  $G$ ,  $R$ ,  $J$ . This usage, which we shall presently find to be of practical

<sup>1</sup> However interpreted, this 'sphericity' is only approximate, as we know from chemistry and surface-tension. But for many purposes 'it is possible to couch the experimental conclusions in terms of the very simple picture of elastic spheres of a given diameter, the diameter in such case being the statistical average distance of approach of the molecules for the average velocity. An analysis expressed in terms of such a picture is entirely justified as it influences the results but little, while it simplifies calculation and interpretation greatly.'—L. Loeb, *Kinetic Theory of Gases*, 1927, p. 524.



importance, is justified by the fact that our argument is based upon the general theorem for tautomeric products.

We next make the assumption that, in addition to the characteristic  $w$ , there are two other characteristics  $a'$  and  $b'$  whose measure-ratios are

$$\begin{aligned} A' &= V^r(R\Theta)^y W^z = L^{3x+2y} W^{y+z} T^{-2y} \\ B' &= V^l(R\Theta)^m W^n = L^{3l+2m} W^{m+n} T^{-2m} \end{aligned}$$

Hence  $L$  and  $T$ , or  $V$  and  $(R\Theta)$ , being expressible in terms of  $A'$ ,  $B'$ , and  $W$ , are uniquely determined. Instead of these two general characteristics, it will be more convenient to take  $a$  and  $b$  such that

$$\begin{aligned} A &= A'/W^z = V^x(R\Theta)^y \\ B &= \left( B' W^{\frac{mz-ly}{y}} A'^{-\frac{m}{y}} \right)^{\frac{y}{ly-mx}} = V \end{aligned}$$

Let  $q$  be any resultant property. Then its measure-ratio

$$\begin{aligned} Q &= L^z M^\beta T^\gamma = W^{\beta+\frac{\gamma}{2}} V^{\frac{\alpha+\gamma}{3}} (R\Theta)^{-\frac{\gamma}{2}} \\ &= W^{\frac{2\beta+\gamma}{2}} A^{-\frac{\gamma}{2y}} B^{\frac{\alpha+\gamma}{3}-\frac{x\gamma}{2y}} \end{aligned}$$

That is,  $Q$  may be expressed either in the form  $W^{x_1} V^{x_2} (R\Theta)^{x_3}$  or in the form  $W^{x_1} A^{x_4} B^{x_5}$ .

As a particular case of  $q$  take the pressure  $p$ , and for probasic quantities choose the characteristics  $w$ ,  $a$ ,  $b$ , so that  $R\Theta = A^{\frac{1}{y}} B^{-\frac{x}{y}}$ ,  $V = B$ ,  $P = A^{\frac{1}{y}} B^{-(1+\frac{x}{y})}$ . Then the equation  $f(p, a, b, w, v, r\theta) = 0$  can be expressed in the form

$$f\left(\frac{p}{a^{\frac{1}{y}b^{-(1+\frac{x}{y})}}}, \frac{v}{b}, \frac{r\theta}{a^{\frac{1}{y}b^{-\frac{x}{y}}}}\right) = 0$$

Now let

$$p_0 = \lambda a^{\frac{1}{y}b^{-(1+\frac{x}{y})}}, v_0 = \mu b, r\theta_0 = \nu a^{\frac{1}{y}b^{-\frac{x}{y}}}$$

where  $\lambda$ ,  $\mu$ ,  $\nu$  are arbitrary multiples fixed for all substances. Then we have

$$F(\lambda p/p_0, \mu v/v_0, \nu \theta/\theta_0) = 0$$

or

$$\phi(p/p_0, v/v_0, \theta/\theta_0) = 0$$

where  $\phi$  is the same function for all gases and liquids. And if we choose the multipliers so that  $F(\lambda, \mu, \nu) = 0$ , then  $p = p_0$ ,  $v = v_0$ ,  $\theta = \theta_0$  represent one possible state of the substance; we may call it the 'standard' state. Since more than one set of multipliers satisfy the equation  $F(\lambda, \mu, \nu) = 0$ , there will be several possible standard states. One of these states, the critical state, is particularly important; it is identifiable independently of any knowledge of  $a$  and  $b$ . It is defined analytically by  $\delta p/\delta v = \delta^2 p/\delta v^2 = 0$ ,  $\theta$  being kept constant, i.e. it is represented by the point of inflexion on the isothermal curve. Since we can put

$$p/a^{\frac{1}{\nu}}b^{-(1+\frac{x}{y})} = \phi_1(v/b, r\theta/a^{\frac{1}{\nu}}b^{-\frac{x}{y}})$$

$$\delta p/\delta v = 0 \text{ gives } \phi_2(v/b, r\theta/a^{\frac{1}{\nu}}b^{-\frac{x}{y}}) = 0$$

$$\text{and } \delta^2 p/\delta v^2 = 0 \text{ gives } \phi_3(v/b, r\theta/a^{\frac{1}{\nu}}b^{-\frac{x}{y}}) = 0$$

These latter two equations have for solution

$$v_c = \mu_c b, r\theta_c = \nu_c a^{\frac{1}{\nu}}b^{-\frac{x}{y}}$$

where  $\mu_c$  and  $\nu_c$  are independent of the particular values of  $a$  and  $b$ . Hence

$$p_c = \lambda_c a^{\frac{1}{\nu}}b^{-(1+\frac{x}{y})}$$

where <sup>1</sup>

$$\lambda_c = \phi_1(\mu_c, \nu_c)$$

We will denote the 'reduced' pressure, volume and temperature ( $p/p_c, v/v_c, \theta/\theta_c$ ) by the capital letters P, V, T, as they are no longer likely to be confounded with what we have hitherto called measure-ratios.<sup>2</sup> Our result may then be summed up in the equation  $\phi(P, V, T) = 0$ , where  $\phi$  is a general function independent of the particular substance. As is well known, this is very approximately true for gases and liquids. It should be noted that our proof is quite independent of any particular form of the equation of state; in particular our  $a$  and  $b$  need not be identified with the quantities which Van der Waals designates by these letters.

Reverting to the general resultant property  $q$ , we have  $q = f(a, b, w, v, r\theta)$ . Taking  $w, v, r\theta$  as probasic quantities, we have

$$q/w^{x_1}v^{x_2}(r\theta)^{x_3} = F(a/v^x(r\theta)^{\nu}, b/v)$$

Now  $b/v = (v_c/v)/\mu_c = 1/\mu_c V$  and  $a = b^x(r\theta_c/v_c)^{\nu}$  so that

$$a/v^x(r\theta)^{\nu} = 1/\mu_c^x \nu_c^{\nu} V^x T^{\nu}$$

That is

$$q/w^{x_1}v^{x_2}(r\theta)^{x_3} = \psi(V, T)$$

Now  $q$  does not depend on the *total* mass and volume of the gas, provided they are large enough for the application of statistical laws. It depends on the molecular quantities:  $m, v_m = vm_{\text{H}}, g\theta$ . It is therefore preferable to write the equation in the form

$$q/m^{x_1}(vm_{\text{H}})^{x_2}(g\theta)^{x_3} = \phi(V, T)$$

or

$$q/w^{x_1}v^{x_2}\theta^{x_3} = A\phi(V, T)$$

where  $A = m_{\text{H}}^{x_1+x_2}g^{x_3}$ . In the sequel we shall generally denote monometric constants (independent of V and T) by the letters A, B, C, &c. Func-

<sup>1</sup> It follows that  $r\theta_c/p_c v_c = \nu_c/\lambda_c \mu_c$  is the same for all substances. It is found to be about 3.7, whereas Van der Waals's theory gives  $8/3 = 2.67$ .

<sup>2</sup> As a matter of fact, we have here a *third* interpretation of 'dimensions', namely, the intrinsic measure of a quantity or the ratio of its measure to the measure of a particular instance within the system. And we could have investigated this interpretation independently. This use of the letter T for  $\theta/\theta_c$  is so convenient that it is worth risking the chance of confusion with our former use of T.

tions of V and T, which are symmetric in the sense of being the same for all substances, will be denoted by  $\phi$ ,  $\psi$ ,  $f$ , &c.

The general formula which we have just proved has many important advantages :

- (a) It is independent of any particular equation of state.
- (b) It provides a simple logical basis for a fruitful application of so-called dimensions.
- (c) It enables us to co-ordinate many apparently diverse empirical formulae.
- (d) It 'explains' the very different orders of magnitude of various quantities, for  $\phi$  being a resultant operational function is of the order unity.<sup>1</sup>
- (e) It gives a clear dynamical meaning to 'corresponding states' and a simple proof for many relations connecting them.<sup>2</sup>

We can even extend this result. By assuming a further characteristic  $c$ , we can explain deviations from the law of corresponding states. We then have

$$A = V^{\gamma}(R\Theta)^{\nu}, B = V$$

$$C = W^{\nu_1} V^{\nu_2} (R\Theta)^{\nu_3} = W^{\nu_1} A^{\frac{\nu_2}{\nu_1}} B^{\nu_3 - \frac{\nu_2}{\nu_1}}$$

so that  $W = A^{\alpha} B^{\beta} C^{\gamma}$ , where  $\alpha = -\nu_3/\nu_1$ ,  $\beta = \nu_2/\nu_1$ ,  $\gamma = 1/\nu_1$ .

We then deduce as before

$$p^1 = \phi_1(v', \theta', w')$$

where  $p' = p/a^{\frac{1}{\nu}} b^{-\left(1+\frac{\alpha}{\nu}\right)}$ ,  $v' = v/b$ ,  $\theta' = r\theta/a^{\frac{1}{\nu}} b^{-\frac{\alpha}{\nu}}$ ,  $w' = w/a^{\alpha} b^{\beta} c^{\gamma}$ . The conditions for the critical point give

$$\phi_2(v', \theta', w') = \phi_3(v', \theta', w') = 0$$

Putting  $v' = \mu_c$ ,  $\theta' = \nu_c$ , we deduce that  $\lambda_c$ ,  $\mu_c$ ,  $\nu_c$  are no longer constant but functions of  $w'$ .

We similarly find

$$\phi(P, V, T, w') = 0$$

and

$$q/w^{\nu_1} v^{\nu_2} (r\theta)^{\nu_3} = \psi(V, T, w')$$

where  $w' = w/a^{\alpha} b^{\beta} c^{\gamma}$ .

However, we shall prescind from this complication and assume that the law of corresponding states is true, the fitting of any particular equation to each substance requiring a slight adjustment of the constants involved. Hence in examining a few of the applications of the theorem we have proved, we shall content ourselves with average values, it being understood that there are individual deviations (especially in the case of the permanent

<sup>1</sup> For example, taking  $q$  to be the pressure, the equation becomes  $p/v^{-1}\theta = gm_H^{-1}\phi$  or  $pv/r\theta = 3\phi/2$ . And since  $pcv_c/r\theta_c$  is about 3.7, it follows that in this case  $\phi(1, 1)$  is about 2.5.

<sup>2</sup> For instance, Kleeman gives an elaborate argument and even tabulates experimental results to prove that the ratio of surface-tension ( $s$ ) to surface-energy ( $\sigma$ ) has the same value for all liquids at corresponding temperatures.—*Phil. Mag.*, 1909, 18, 495 ff. From our theorem it is obvious that  $s/\sigma$ , being symmetric, is equal to  $\phi(V, T)$ . In his book (*Atomic and Molecular Forces*, 1931, p. 33) he deduces  $r\theta_c/p_c v_c = \text{const.}$  from 'the law of molecular attraction and the laws of thermodynamics'.

gases and liquid alcohols). Also several of the empirical expressions for  $\phi$  do not hold in the near neighbourhood of the critical point.

### Surface Tension

Surface tension ( $s$ ) being force/distance, its measure-ratio is  $S = M/T^2 = G\Theta V^{-\frac{2}{3}}$ . (No ambiguity arises from the use of  $T$  for time-ratio in logometric formulae.) Hence  $sv_m^{\frac{2}{3}}/g\theta = \phi$ , or  $sv^{\frac{2}{3}}/\theta = A\phi$ , where  $A = g/m_H^{\frac{2}{3}} = 0.934 = \text{say, } 1$ . We therefore have the formula

$$sv^{\frac{2}{3}}/\theta = \phi \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The function  $\phi$  must be determined empirically; for ordinary pressures it can be considered to be a function of  $T$  alone. R. Eötvös<sup>1</sup> was the first to prove this formula from the theory of corresponding states, though his proof is not very clear. He also claimed to prove experimentally that  $sv^{\frac{2}{3}} = 2.27(\theta_c - \theta)$ ; which is equivalent to taking  $\phi$  as  $2.27(1-T)/T$ . But we shall presently see that a more accurate expression is now known.<sup>2</sup>

From (1) we deduce at once that

$$sv_c^{\frac{2}{3}}/\theta_c = TV^{-\frac{2}{3}}\phi = \text{say, } \psi$$

And it has been shown<sup>3</sup> that  $\psi = C(1 - T)^n$ , where on the average  $C = 5.08$  and  $n = 1.234$ , or in round numbers  $C = 5$ ,  $n = 6/5$ . Thus

$$S = s_0(1 - T)^{1.2}, \text{ where } s_0 = 5\theta_c v_c^{-\frac{2}{3}} \quad . \quad . \quad . \quad (2)$$

If in this formula we expand the right-hand side and put  $T = (t + 273)/\theta_c$ , we find

$$s = a - bt + ct^2 + \dots$$

where the coefficients contain powers of  $\theta_c$ . An empirical formula of this type has been proposed by Young, Gross, and Harkins for water ( $10^\circ$  to  $60^\circ$ ) and for benzene ( $20^\circ$  to  $60^\circ$ ).<sup>4</sup>

<sup>1</sup> *Ann. Physik.*, 1886, 27, 454. 'The theoretical grounds on which he founds the law are, in the present state of physics, somewhat transcendental.'—Sutherland, *Phil. Mag.*, 1889, 27, 306. 'The theoretical researches made up to the present to interpret this law are hardly satisfactory.'—Brillouin, *Compt. rend.*, 1925, 180, 1249. 'Eötvös deduced his equation theoretically from considerations of corresponding states of liquids of similar constitution, which are rather difficult to follow.'—Adam, *Physics and Chemistry of Surfaces*, 1930, p. 154. The particular form for  $\phi$  is purely empirical. But I have now shown that equation (1) follows from the assumption of molecular similarity; also  $\phi(1) = 0$  and  $\phi(0) \rightarrow 1$ .

<sup>2</sup> The formula of Ramsay and Shields

$$sv^{\frac{2}{3}} = a(\theta_c - \theta - 6)$$

is now known to be incorrect. Their results for  $s$  are too low owing to underestimation of capillary rise and should be increased by about 3.16 per cent. Cf. Richards and Coombe, *J. Amer. Chem. Soc.*, 1915, 37, 1675; Sugden, *J. Chem. Soc.*, 1924, 125, 32, 1167.

<sup>3</sup> Van der Waals, *Zeit. phys. Chem.*, 1894, 13, 716. He gave  $n$  but not  $C$ . The latter is taken from M. Katayama, *Science Reports Tohoku Imp. Univ.*, 1916, 4A, 385. The formula was also given by A. Ferguson, *Phil. Mag.*, 1916, 31, 37; *Trans. Farad. Soc.*, 1923, 19, 408. A formula  $s = s_0(1 - \theta/a)^n$  has been proposed for liquid nitrous oxide ( $s_0 = 72.8$ ,  $a = 311.8$ ,  $n = 1.26$ ) by Quinn and Wernimont, *J. Amer. Chem. Soc.*, 1930, 52, 2728; and for liquid fluorhydric acid ( $s_0 = 40.7$ ,  $a = 503.2$ ,  $n = 1.78$ ) by Simons and Bouknight.—*Ibid.*, 1932, 54, 129.

<sup>4</sup> Cited in Alexander (editor), *Colloid Chem.*, 1926, 1, 260.

Combining equations (1) and (2), we obtain

$$sv^{\frac{2}{3}} = \phi = C\theta_c V^{\frac{2}{3}}(1 - T)^{\frac{2}{3}} \quad . \quad . \quad . \quad (3)$$

Combining this with the expression for  $V$  to be given later (10), we have <sup>1</sup>

$$sv^{\frac{2}{3}} = \frac{5.08\theta_c}{2^{\frac{2}{3}}} \cdot \frac{(1 - T)^{1.2}}{[(1 - T)^{0.3} + 1 - T/2]^{\frac{2}{3}}}$$

Except near the critical point this is indistinguishable from the linear function  $2.01\theta_c(1 - T)$ . This explains why the formula of Eötvös is approximately correct.

Katayama <sup>2</sup> discovered the following interesting formula

$$s[w/(\rho - \rho')]^{\frac{2}{3}} = B\theta_c(1 - T) \quad . \quad . \quad . \quad (4)$$

where  $\rho$  is the density of the liquid and  $\rho'$  that of the saturated vapour,  $B$  being on the average 2.04 (Katayama) or 2.210 (Morino).

Comparing (3) and (4), we obtain

$$[(\rho - \rho')/\rho]^{\frac{2}{3}} = (C/B)(1 - T)^{\frac{2}{3}}V^{\frac{2}{3}}$$

Since  $V = v/v_c = \rho_c/\rho$ , this can be expressed as

$$(\rho - \rho')/\rho_c = (C/B)^{\frac{3}{2}}(1 - T)^{\frac{5}{2}}$$

Writing  $D$  and  $D'$  for  $\rho/\rho_c$  and  $\rho'/\rho_c$  and putting  $C = 5.08$ ,  $B = 2.04$ , this becomes

$$D - D' = 3.93(1 - T)^{0.3} \quad . \quad . \quad . \quad (5)$$

The elimination of  $T$  from (2) and (4) results in the important formula <sup>3</sup>

$$\begin{aligned} s/(\rho - \rho')^4 &= A\theta_c/w^{\frac{2}{3}}\rho_c^{\frac{1}{3}} \\ &= A\theta_c v_c^{\frac{1}{3}}/w^4 \quad . \quad . \quad . \quad (6) \end{aligned}$$

where  $A = B^6/C^5 = 0.0213$ . Direct experiment gives a better value for  $A$ , namely, 0.0274.

The quantity

$$q \equiv ws^{\frac{2}{3}}/(\rho - \rho') = 0.41\theta_c^{\frac{1}{3}}v_c^{\frac{2}{3}} \quad . \quad . \quad . \quad (7)$$

has been called the *parachor* ('comparative volume') and is asserted to possess a curious theoretical importance. Whatever be the merits of this quantity in chemistry, its physical foundations are rather shaky. We are told that

the quantity has the dimensions of volume and, at low temperatures where  $\rho'$  becomes very small, is in fact the molecular volume. Hence a comparison of  $q$  for different substances is a comparison of molecular volumes at temperatures at which the liquids have the same surface tension. . . . If  $q$  is a true measure of the molecular volume, it should bear an approximately constant ratio to the critical volume.<sup>4</sup>

<sup>1</sup> Ferguson and Miller, *Proc. Phys. Soc.*, 1934, 46, 141.

<sup>2</sup> *Loc. cit.*, p. 376. Morino, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), Dec. 1933, No. 476, p. 60.

<sup>3</sup> Macleod independently gave  $s = c(\rho - \rho')^4$  for a given substance.—*Trans. Far. Soc.*, 1923, 19, 38. Cf. Ferguson (*ibid.*, p. 408), who takes  $B = 2.089$  and  $C = 4.971$ . Ferguson and Kennedy, *Trans. Far. Soc.*, 1936, 32, 1477, give  $s = \text{const.}(\rho - \rho')^4$ , where  $a$  is constant for any one liquid: ethane, 3.846; propane, 4.4; benzene, 3.82 to 3.97, according to different observers. These refinements, i.e. the effecting of slight adjustments to suit each individual substance, are beyond the scope of the present chapter.

<sup>4</sup> S. Sugden, *J. Chem. Soc.*, 1924, 125, 1177. Cf. N. K. Adam (*loc. cit.*, p. 165): 'The parachor is much the most satisfactory convention as to molecular volumes, truly

Now it is quite clear from inspection that  $q$  has *not* the dimensions (measure-ratio) of volume :

$$Q = MS^{\frac{1}{2}}/D = M^{\frac{1}{2}}L^{\frac{3}{2}}/T^{\frac{1}{2}} = \Theta^{\frac{1}{2}}V^{\frac{2}{3}}$$

Obviously the word 'dimensions' in this connection has no reference to a change of units, only to a comparison of two dynamically similar systems. Since  $s$  is not symmetric,  $vs^{\frac{1}{2}}$  cannot have the measure-ratio of  $v$ ; besides, according to the argument<sup>1</sup> just cited,  $vs^n$ , where  $n$  is an arbitrary index, might with equal propriety have been taken as the 'parachor'. And if we really<sup>2</sup> want the 'the molecular volume' we must consider the expression  $q' = vs^{\frac{1}{2}}$ . Now from formulae (7) and (10) we find

$$\begin{aligned} q' &= s^{\frac{1}{2}}w/\varrho \\ &= \frac{0.82\theta_c^{\frac{1}{2}}v_c^{\frac{2}{3}}(1-T)^{0.3}}{0.91(1-T)^{0.3} + 1 - T/2} \end{aligned}$$

which is a rather complicated expression, only approximately independent of  $T$ .

Moreover, the constancy of  $q/v_c$  (supposed to be 0.78) is more than doubtful; the constancy of this ratio would imply that  $\theta_c^3/v_c^2$  is the same for all substances—which is only very roughly true. The following table is instructive<sup>3</sup>:

	$q$	$\theta_c$	$v_c$	$q/v_c$	$q/\theta_c^{\frac{1}{2}}v_c^{\frac{2}{3}}$
Hydrogen . . .	35.1	32.2	72.4	0.54	0.46
Benzene . . .	206.3	561.5	256.1	0.81	0.42
Chlorobenzene . .	244.5	632.5	307.8	0.80	0.41
Carbon tetrachloride	219.9	556.14	276.1	0.80	0.42
Methyl formate . .	138.6	487.0	172.0	0.81	0.41
Ethyl acetate . .	217.1	523.1	286.0	0.76	0.41
Bromine . . .	132.1	575.2	135.4	0.98	0.42
Oxygen . . .	54.0	155.0	74.4	0.73	0.43
Nitrogen . . .	60.4	126.5	88.8	0.68	0.43

The rough constancy of  $q/v_c$  here displayed shows us why the parachor is approximately additive in compounds, for  $v_c$  is already known to have this property.<sup>4</sup>

comparable for different substances, which has yet been found; and its rational basis is that the compounds are compared under similar conditions of surface tension, which is nearly the same as comparing them under equal degrees of self-compression by the inter-molecular cohesional forces.'

<sup>1</sup> 'A measure of the molecular volume at temperatures at which different liquids have the same surface tension.'—Lowry and Sugden, *Class Book of Physical Chemistry*, 1929, p. 73.

<sup>2</sup> The parachor 'is in fact a molecular volume'.—Lowry, *Nature*, 1930, 125, 364.

<sup>3</sup> Sugden, *J. Chem. Soc.*, 1924, 125, 1178, 1188; *Parachor and Valency*, 1930, p. 31. The last column has been added; it was already given by Ferguson, *Nature*, 1930, 125, 597. Sugden admitted that 'Dr. Ferguson's relation is undoubtedly more accurate'. But since then Ferguson and Kennedy (*loc. cit.*, p. 1479) have proposed  $q = 0.157\theta_c^{\frac{1}{2}}v_c^{\frac{2}{3}}$ , which is incompatible with the theory of corresponding states. In the table  $v_c$  for  $N_2$  is given as 88.8 (instead of the atomic value 44.4); and  $v_c$  for  $H_2$  is put as 72.4 instead of 46.9, since  $\varrho_c = 0.0310$ .—Pickering, *Sci. Papers, Bureau of Standards*, 1926, 21, 613.

<sup>4</sup> Or, extrapolating (5) to  $T = 0$ , we have  $v_c = 3.93v_0$ ; hence  $q = 0.78v_c = 3.1v_0$ . And  $v_0$  is recognized as approximately additive.

The surface-energy ( $\sigma$ ) is related to the surface-tension ( $s$ ) by the formula  $\sigma = s - \theta ds/d\theta$ . Hence from (2)

$$\begin{aligned}\sigma &= s(1 + T/5)/(1 - T) \\ &= C\theta_c v_c^{-\frac{1}{3}}(1 - T)^{0.2}(1 + T/5)\end{aligned}\quad . \quad . \quad . \quad (8)$$

Using (4) we find

$$\sigma v^{\frac{1}{3}}/\theta_c = B(1 + 0.2T)[(\varrho - \varrho')/\varrho]^{\frac{1}{3}}$$

If we evaluate the right-hand side for chlorobenzene at the two temperatures  $150^\circ$  and  $270^\circ$ , we obtain 2.312 and 2.322. The function is thus approximately constant.<sup>1</sup> Or, utilizing (5) and (10), we have<sup>2</sup>

$$\sigma v^{\frac{1}{3}}/\theta_c = 2^{\frac{1}{3}}B \cdot \frac{(1 - T)^{0.2}(1 + 0.2T)}{[(1 - T)^{0.3} + 1 - 0.5T]^{\frac{1}{3}}}$$

which is found to vary only slightly with  $T$ .

In testing empirical formulae it is important to remember that temperature ranges which appear large when estimated in degrees Centigrade may be narrow when expressed in reduced temperatures. Thus according to R. D. Kleeman,<sup>3</sup>  $\sigma/\varrho^{\frac{2}{3}}\theta$  is a constant independent of the temperature for each substance. From our previous formulae we easily derive

$$\frac{\sigma}{(\varrho - \varrho')^{\frac{2}{3}}\theta} = \frac{B^{\frac{1}{3}}}{c^{\frac{2}{3}}v_c^{\frac{2}{3}}\varrho_c^{\frac{2}{3}}} \cdot \frac{1 + 0.2T}{T(1 - T)^{0.4}}$$

The values of  $\sigma/\varrho^{\frac{2}{3}}\theta$  for benzene at the lowest and highest temperatures given by Kleeman ( $80^\circ$  and  $240^\circ\text{C}$ ., i.e.  $T = 0.63$  and  $T = 0.90$ ) are 0.254 and 0.274. Taking  $B = 2.04$  and  $C = 5.08$ , the right-hand side of the equation just given becomes 0.265 and 0.356 at these two limits; while a direct calculation of  $\sigma/(\varrho - \varrho')^{\frac{2}{3}}\theta$  gives 0.260 and 0.356. This proposal of Kleeman is an example of an attempt to base a law on too narrow a range of temperature ( $0.90 - 0.63 = 0.27$ ). The proper measure of temperature, to which terms such as 'high' and 'low' can be applied, is the tautomeric quantity  $T = \theta/\theta_c$ . Thus the temperature  $-243^\circ$  (or  $30^\circ\text{K}$ ) is high for hydrogen ( $T = 0.9$ ) but low for benzene ( $T = 0.05$ ).

Any other proposed laws involving  $s$  or  $\sigma$  can be similarly investigated by the 'dimensional' method here outlined. For instance,  $s/pv^{\frac{1}{3}}$  and  $s/p^{\frac{1}{3}}\theta^{\frac{1}{3}}$  are clearly symmetric.<sup>4</sup> In equation (2) put  $\theta_c = 3.7p_c v_c/r$ ,  $p_c = 10^6 p'_c$  (atmospheres),  $T = 0.5$  (melting-point) and we obtain  $s = p'_c v_c^{\frac{1}{3}}/10.3$ , which is Dutoit's formula.<sup>5</sup> Similarly, if  $\beta$  is the compressibility,  $\beta\theta/v^{\frac{1}{3}} = A\phi$ , where  $A$  is  $m_H^{\frac{1}{3}}$  or  $1.16 \times 10^{-8}$ . But non-homogeneous formulae, which contradict the principle of corresponding states, should be avoided. Thus Richards and Matthews<sup>6</sup> assert that  $s^{\frac{1}{3}}\beta = 2.5 \times 10^{-6}$  for a large number of unassociated liquids over ordinary ranges of temperature. But this product is not symmetric, much less monometric; it is merely a rough approximation,  $\beta$  being taken at its average value for 100

<sup>1</sup> Bennett and Mitchell, *Zeit. phys. Chem.*, 1913, 84, 475.

<sup>2</sup> Ferguson and Miller, *Proc. Phys. Soc.*, 1934, 46, 146.

<sup>3</sup> *Phil. Mag.*, 1909, 18, 500.

<sup>4</sup> Eötvös, *loc. cit.*, pp. 453 f.

<sup>5</sup> Dutoit-Fridrich, *J. chimie phys.*, 1909, 7, 169.

<sup>6</sup> *Zeit. phys. Chem.*, 1908, 61, 449.

to 500 atm. A similar remark applies to the equation  $^1 1/\beta_s = 2.5 \times 10^{-9}$  at  $0^\circ\text{C}$ .; this merely means that  $v_0^3$  is roughly constant for organic liquids. The number of such possible formulae is legion; and they are of no particular interest.

### Density

We can be briefer in examining the relations satisfied by other properties of liquids and gases. Let  $\varrho$  be the density of a liquid under the saturation-pressure ( $p$ ), and therefore approximately under atmospheric pressure, at temperature  $\theta$ ,  $\varrho'$  the density of the saturated vapour at this pressure and temperature,  $D \equiv \varrho/\varrho_c = 1/V$ ,  $D' \equiv \varrho'/\varrho_c = 1/V'$ ,  $P \equiv p/p_c$ . Then  $D = \psi(P, T) = \phi(T)$ , since  $P = f(T)$ ; similarly  $D' = \phi'(T)$ .

The Cailletet-Mathias rule of the rectilinear diameter in the density-temperature curves for liquid and vapour is equivalent to the formula

$$(\varrho + \varrho')/2\varrho_c \equiv (D + D')/2 = B - CT \quad (9)$$

This has been verified for numerous substances <sup>2</sup> and is found to hold very accurately except very near the critical point.  $B$  is never very different from 2 (the extreme limits being 1.79 and 2.07), and  $C$  may be taken as  $B - 1$ . This last approximation amounts to assuming that the formula is valid right up to the critical point ( $\varrho = \varrho' = \varrho_c$ ).<sup>3</sup>

We have already found the equation <sup>4</sup>

$$D - D' = 2A(1 - T)^m \quad (5)$$

where  $A$  is 1.965 and  $m = 0.3$ . For greater accuracy special values of these constants must be 'fitted' for each substance, but they will closely cluster round these average values. From (9) and (5) we obtain

$$D = A(1 - T)^m + B - CT \quad (10)$$

For example, putting  $T = 0.6$ , we find  $\varrho_c = 0.3592\varrho$ .

Also

$$\begin{aligned} \alpha &\equiv \frac{1}{v} \frac{dv}{d\theta} = \frac{-1}{\varrho\varrho_c} \frac{d\varrho}{dT} \\ &= \frac{1}{\varrho_c} \cdot \frac{mA(1 - T)^{m-1} + C}{A(1 - T)^m + B - CT} \end{aligned}$$

Taking  $A = 2$ ,  $B = 1.9$ ,  $C = 0.9$ ,  $m = 0.3$ , we find:  $\alpha = 0.4/\theta_c$  when  $T = 0$ ,  $\alpha = 1/3\theta_c$  when  $T = 0.5$ ,  $\alpha = 0.9/\theta_c$  when  $T = 1$ . Expanding to the first power of  $\theta$ , we find

$$\alpha = (\theta_c + 0.2\theta)/(2.5\theta_c - \theta)$$

<sup>1</sup> Hammick, *Phil. Mag.*, 1921, 41, 31. Or we might put it thus:  $[\beta_s] = L$ , and  $d$  (molecular diameter) is about  $4.5 \times 10^{-8}$  cm. for organic liquids.

<sup>2</sup> Data in von Jüptner, *Zeit. phys. Chem.*, 1913, 58, 1 ff.

<sup>3</sup> If we put  $B = 2$ , we obtain  $\varrho + \varrho' = 4\varrho_c(1 - T/2)$ .—Davies, *Phil. Mag.*, 1912 23, 657. If we neglect  $\varrho'$  we obtain a formula valid only at low temperatures:  $\varrho/\varrho_c = 4 - 2T$ . Hence if  $\varrho_1$  and  $\varrho_2$  are the values of the density of a liquid at low temperatures  $\theta_1$  and  $\theta_2$ ,  $\theta_c = (\theta_2\varrho_1 - \theta_1\varrho_2)/2(\varrho_1 - \varrho_2)$ .—Thorpe and Rücker, *J. Chem. Soc.*, 1884, 45, 135. At temperatures not far from the critical we can put  $\varrho' = \varrho$ ; hence  $\varrho/\varrho_c = 2 - T$ .—Berthelot, *Compt. rend.*, 1899, 128, 606.

<sup>4</sup> Cf. Lahr, *Die Zustandsgleichung*, 1924, p. 345; Ferguson and Miller, *loc. cit.*, p. 142.



Neglecting  $\varrho'$ , we obtain from (5)

$$v = v_c/4(1 - T)^{0.3} \quad . \quad . \quad . \quad (10a)$$

and from (9)

$$v = v_c/2(2 - T) \quad . \quad . \quad . \quad (10b)$$

whence we easily obtain two approximate expressions<sup>1</sup> for  $\alpha$ :

$$\begin{aligned} \alpha &= 0.3/(\theta_c - \theta) \\ \alpha &= 1/(2\theta_c - \theta) \end{aligned}$$

Using the latter expression, (10b) becomes

$$v = \frac{1}{2}v_c\alpha\theta_c = v_02\alpha\theta_c \quad . \quad . \quad . \quad (10c)$$

where  $v_0 = v_c/4$  is extrapolated from (10ab) by putting  $T = 0$ .

It should be observed that the usual average coefficient of expansion is defined by  $v = v_0(1 + at)$ , where  $t$  is the temperature centigrade and  $v_0$  is the volume at  $0^\circ$  (*not* at the absolute zero). Hence

$$\alpha = \frac{1}{v} \frac{dv}{dt} = a \frac{v_0}{v} = \frac{a}{1 + at} = a(1 - at)$$

approximately. Using (10a) we find  $a = 0.3/t_c$ , using (10b) we find  $a = 1/(2t_c + 273)$ . These are useful approximations.

The following equations express in 'reduced' form some other relations which have been found. The first<sup>2</sup> is, ( $\ln$  denoting natural log),

$$D^{\frac{1}{3}} - T \ln D^{\frac{1}{3}} = D'^{\frac{1}{3}} - T \ln D'^{\frac{1}{3}} = (3 - T)/2$$

whence we derive

$$1/V^{\frac{1}{3}} - 1/V'^{\frac{1}{3}} = \frac{1}{3}T \ln(V'/V) \quad . \quad . \quad (11)$$

Another<sup>3</sup> is

$$T \ln(V'/V) = A[1/(V - B) - 1/(V' - B)]$$

where  $A = 0.194n = 0.728$  approx. ( $n \equiv r\theta_c/p_c v_c$ ), and  $B = 0.169$ . From these two we deduce

$$1/V^{\frac{1}{3}} - 1/V'^{\frac{1}{3}} = \frac{1}{3}A[1/(V - B) - 1/(V' - B)] \quad . \quad (12)$$

### Latent Heat

We now turn to the latent heat ( $\lambda$ ) of a liquid at temperature  $\theta$ , i.e. the amount of heat necessary to convert unit mass of the liquid into vapour at the same temperature;  $w\lambda$  is the heat required to vaporize one mol. The values, which are not known very accurately,<sup>4</sup> are generally calculated from the thermodynamic equation

$$jw\lambda = (v' - v)\theta dp/d\theta \quad . \quad . \quad . \quad (13)$$

The energy used in vaporizing a mol is  $jw\lambda$ ; subtracting from this the portion used in the external work  $p(v' - v)_1$  we obtain  $jw\lambda'$ , where  $\lambda'$  is the internal

<sup>1</sup> Davies gave  $1/(2\theta_c - \theta)$ .—*Phil. Mag.*, 1912, 24, 416. Thatté gave  $1/(2.5\theta_c - 2\theta)$ .—*Ibid.*, 1929, 7, 887.

<sup>2</sup> Kleeman, *Phil. Mag.*, 1911, 21, 327; Shaxby, *ibid.*, 1926, 2, 1131.

<sup>3</sup> Horiuti, *Sci. Papers, Inst. Phys. Chem. Research* (Tokyo), 1931, 15, 89.

<sup>4</sup> Sutton, *Phil. Mag.*, 1915, 29, 594.

latent heat. Since  $p$ ,  $v'$ ,  $v$  are functions of the temperature alone and  $p(v' - v)/r\theta$  is symmetric,<sup>1</sup>

$$jw(\lambda - \lambda') = p(v' - v) = r\theta\phi(T)$$

where

$$\phi(1) = 0.$$

Latent heat being heat/mass, its measure-ratio is

$$[\lambda] = H/M = JH/JM = L^2/JT^2$$

Hence

$$\left[ \frac{m\lambda}{sv_m^{\frac{3}{2}}} \right] = \frac{ML^2/JT^2}{MT^{-2}L^2} = \frac{1}{J}$$

or <sup>2</sup>

$$w\lambda/sv_m^{\frac{3}{2}} = A\phi$$

where

$$A = 1/jm_H^{\frac{3}{2}} = 2.06 = \text{say, } 2$$

Similarly

$$w\lambda/\sigma v^{\frac{3}{2}} = A\psi, \quad w\lambda'/\sigma v^{\frac{3}{2}} = A\phi', \quad w\lambda'/\sigma v^{\frac{3}{2}} = A\psi'$$

where

$$\phi/\psi = \phi'/\psi' = \sigma/s = (1 + 0.2T)/(1 - T)$$

Professor E. T. Whittaker<sup>3</sup> pointed out that  $\sigma/\lambda'\theta$  is a constant for each liquid; and R. Kleeman,<sup>4</sup> by a cumbrous argument of doubtful validity, showed that the constant is proportional to  $w/\theta_c v_c^{\frac{3}{2}}$ . This follows at once from our theorem. For

$$\left[ \frac{\sigma}{\lambda'\theta} \right] = \frac{M/T^2}{H\Theta/M} = \frac{JM}{L^2\Theta}$$

That is

$$\begin{aligned} \sigma/\lambda'\theta &= jm/(v_c m_H)^{\frac{3}{2}} \theta_c \cdot \phi \\ &= w/\theta_c v_c^{\frac{3}{2}} \cdot B\phi \end{aligned}$$

where  $B = jm_H^{\frac{3}{2}} = 0.5$ . Experiment shows that  $B\phi$  is monometric, its average value being 0.557.

Whence

$$w\lambda'/\sigma v_c^{\frac{3}{2}} = 1.795/T$$

Using equation (8) we deduce

$$w\lambda'/\theta = A(1 - T)^{0.2}(1 + 0.2T) \quad . \quad . \quad . \quad (14)$$

where  $A = 1.795 \times 5.08 = 9.12$ . Fig. 8 (III) reproduces this formula with  $A = 9$ . In addition the curves for chlorobenzene and propyl formate are given.<sup>5</sup> It will be observed that the curves can be brought practically into coincidence by an adjustment of the constant  $A$ : for chlorobenzene  $A = 8.78$ , for propyl formate  $A = 7.63$ . The only relevant or practical portion of such curves lies between  $T = 0.5$  and  $T = 1$ ; any lower extension is mere theoretical extrapolation.

<sup>1</sup> Nernst represents  $\phi$  by  $1 - P$ , Berthelot by  $1 + 9P(1 - 6T^{-2})/128T$ .

<sup>2</sup> Waterston thought  $w\lambda/sv^{\frac{3}{2}}$  was constant.—*Phil. Mag.*, 1857, *14*. Eötvös first pointed out that it was symmetric.—*Loc. cit.*, p. 452.

<sup>3</sup> *Proc. Roy. Soc.*, 1908, *81*, 21.

<sup>4</sup> *Phil. Mag.*, 1909, *18*, 43.

<sup>5</sup> The values of  $\lambda'$  are taken from Mills, *J. Amer. Chem. Soc.*, 1909, *31*, 1125 f. The lowest temperature for which  $\lambda$  has been explored is greater than  $T = 0.5$ .

Now in the equation

$$jw\lambda - jw'\lambda' = p(v' - v)$$

the right-hand side may be taken as approximately  $pv' = r\theta$  except very near the critical point. Hence

$$w\lambda/\theta = w'\lambda'/\theta + 1.99 \quad (14a)$$

At the boiling-point ( $T = 2/3$ ) this gives  $w\lambda/\theta = 20.35$ . Which is Trouton's rule. Of course, strictly speaking, the boiling-point is not a corresponding temperature for different substances. For  $p = 1$  atm. cannot have the same ratio to the various critical pressures. For most ordinary substances—with critical pressures ranging from 30 to 60 atm.—we may take  $T_b = 0.64$  and  $V_b = 0.38$ .

K. Watson<sup>1</sup> plotted  $Cw\lambda/\theta$  against  $T$  and showed that by varying the constant  $C$  for different substances the points may be made to lie on one curve. This is reproduced in Fig. 9 (III).

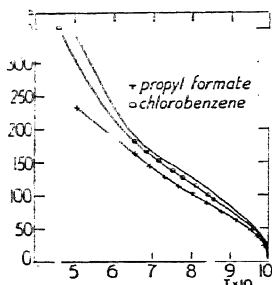


FIG. 8 (III)

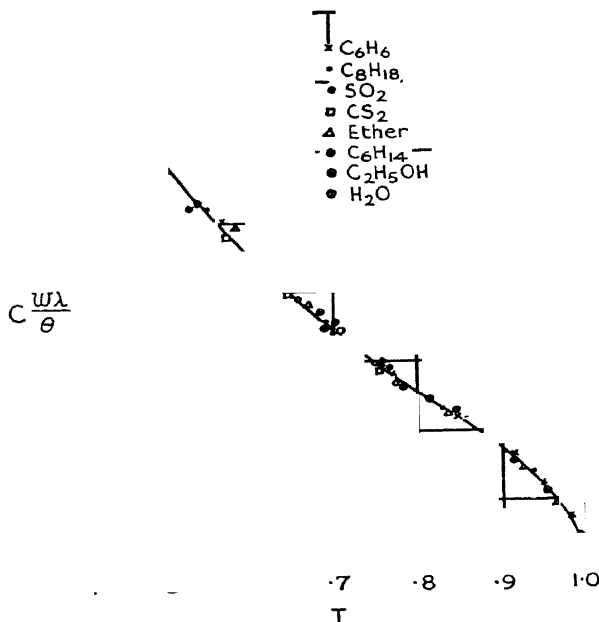


FIG. 9 (III)

From equations (2) and (14) we have

$$w\lambda'/s = 1.795v_c^2(1 + 0.2T)/(T(1 - T))$$

<sup>1</sup> *Ind. Eng. Chem.*, 1931, 23, 362.

or

$$w\lambda'/sv^{\frac{2}{3}} = 1.8V^{-\frac{2}{3}}(1 + 0.2T)/T(1 - T)$$

Taking  $T = 2/3$ ,  $V = 3/7$  at the boiling-point, we find 16.2 for the right-hand side, which accords with the experimental results for the left-hand side.<sup>1</sup>

From (5) and (13) we deduce <sup>2</sup>

$$\frac{\lambda'}{\varrho - \varrho'} = \frac{9.12\theta_c(1 + 0.2T)T}{3.93w\varrho_c(1 - T)^{0.1}}$$

Dieterici <sup>3</sup> has proposed the formula

$$w\lambda'/\theta = C \ln(\varrho/\varrho') = C \ln(V'/V)$$

where  $C = (2 - 1/n)r/j$ ,  $n$  being  $r\theta_c/p_c v_c$ ; putting  $n = 3.75$ , this gives  $C = 3.44$ .

Mills <sup>4</sup> has given the formula

$$\lambda'/( \varrho^{\frac{1}{3}} - \varrho'^{\frac{1}{3}} ) = 3r\theta_c(2 - 1/n)/jw\varrho_c^{\frac{1}{3}}$$

or

$$w\lambda'/\theta = 3C(V^{-\frac{1}{3}} - V'^{-\frac{1}{3}})/T$$

Comparing these with equations (11) and (12), we have

$$\begin{aligned} w\lambda'/\theta_c &= CT \ln(V'/V) = 3C(V^{-\frac{1}{3}} - V'^{-\frac{1}{3}}) \\ &= CA[1/(V - B) - 1/(V' - B)] \end{aligned}$$

where  $A = 0.194n$ ,  $C = (2 - 1/n)r/j$ ,  $B = 0.169$ . Neglecting  $1/(V' - B)$ , putting  $T = 2/3$  and  $V = 3/7$  at the b.p. and taking  $n = 3.75$ , we obtain  $w\lambda'_b/\theta_b = 18.1$ .

### Vapour Pressure

A good approximate formula <sup>5</sup> for  $P \equiv p/p_c$  which embodies proposals by different experimenters, is

$$P = T^{-c} e^{a-b/T}$$

or

$$\ln P = a - b/T - c \ln T \quad . \quad . \quad . \quad (15)$$

Putting  $P = T = 1$ , we see that  $a = b$ . Using ordinary logarithms, we have

$$\log p = A - B/\theta - C \log \theta \quad . \quad . \quad . \quad (16)$$

where

$$\begin{aligned} A &= 0.434b + \log p_c + C \log \theta_c \\ B &= 0.434b\theta_c \\ C &= c \end{aligned}$$

<sup>1</sup> Kleeman, *loc. cit.*, p. 506 (16.3 to 17.5).

<sup>2</sup> According to Bakker,  $\lambda'/( \varrho - \varrho' )$  is monometric.—*J. de phys.*, 1897, 6, 584. According to Edser, it is equal to  $a(1 - b\theta^{\frac{1}{3}})$ .—*Fourth Report on Colloid Chemistry*, 1922 p. 69.

<sup>3</sup> *Ann. Physik.*, 1908, 25, 572; 1911, 35, 220; 1920, 62, 75.

<sup>4</sup> *J. Amer. Chem. Soc.*, 1909, 31, 1099, 1116.

<sup>5</sup> Formula (16) was first given by Kirchhoff.—*Ann. Physik.*, 1858, 104, 612. It is worth observing that the formula is a particular case of Guldberg-Waage's law of mass-action.—Becquerel, *Thermodynamique*, 1924, p. 344.

The last term in (15) is usually negligible, in particular for all metals except mercury. So we shall discuss the equation

$$\log p = A - B/\theta \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Differentiating, we have from (13)

$$\frac{b\theta_c}{\theta^2} = \frac{1}{p} \frac{dp}{d\theta} = \frac{jw\lambda}{p(v' - v)\theta} \quad . \quad . \quad . \quad (18)$$

Using the approximate formulae

$$\lambda = \lambda_b(1 - P), \quad p(v' - v) = r\theta(1 - P)$$

where  $\lambda_b$  refers to the boiling-point, we obtain <sup>1</sup>

$$\begin{aligned} b\theta_c &= jw\lambda_b/r \\ B &= (0.434/1.99)w\lambda_b \\ &= 0.22w\lambda_b \end{aligned}$$

If we put  $\theta_b/\theta_c = 2/3$  and  $w\lambda_b/\theta_b = 21$ , we find  $b = 7$  and

$$B = 4.6\theta_b = 3.1\theta_c$$

If in (18), referred to the boiling-point, we put  $p(v' - v) = pv' = r\theta$  (approx.), we have

$$(dp/d\theta)_b = p_b jw\lambda_b/r\theta_b^2 \quad (18a)$$

Or, with  $p_b = 760$ ,

$$\frac{w\lambda_b}{\theta_b} = \frac{\theta_b}{380} \left( \frac{dp}{d\theta} \right)_b$$

The values of  $(dp/d\theta)_b$  will be found tabulated in Young's *Distillation Principles and Processes*, 1922, p. 14. Thus for chlorine ( $\theta_b = 240$ ) the value is 33.2. Hence  $w\lambda_b/\theta_b = 21$ .

Using Nernst's approximate formula

$$p(v' - v) = r\theta(1 - P)$$

we have from (18), on putting  $rb/j = 14$

$$w\lambda/\theta = 14(1 - P)/T$$

On putting  $\theta = \theta_b = \frac{2}{3}\theta_c$ , and  $p = 1$  (i.e. we measure pressures in atmospheres), this becomes

$$w\lambda_b/\theta_b = 21(1 - 1/p_c)$$

This is another statement of Trouton's rule. We can improve it by not using any special value of  $b$  or  $\theta_b/\theta_c$ . For, since

$$\log P = 0.434b(1 - 1/T)$$

we have

$$\frac{w\lambda}{\theta} = \frac{r(1 - P)}{j(1 - T)} \cdot \frac{\log(1/P)}{0.434}$$

And, on putting  $\theta = \theta_b$ ,  $p = 1$ , this gives <sup>2</sup>

$$w\lambda_b/\theta_b = 4.574 \log p_c \cdot (1 - 1/p_c)/(1 - \theta_b/\theta_c) \quad . \quad . \quad (19)$$

<sup>1</sup> According to Mortimer, the slope (i.e.  $B$ ) of the  $(\log p, 1/\theta)$  curve gives  $0.2364w\lambda_b$ . — *J. Amer. Chem. Soc.*, 1922, 44, 1430.

<sup>2</sup> Cederberg, *Die thermodynamische Berechnung chemischer Affinitäten*, 1916, p. 54. The values of  $w\lambda_b/\theta_b$  calculated from this formula are given in brackets after the observed results: helium 5.2 (4.7); hydrogen 12.1 (11.9); nitrogen 17.6 (17.5); oxygen 18.2 (18.3); ammonia 22.8 (22.7); ethyl acetate 21.2 (21.3); water 25.9 (25.1).

This is much better than Trouton's rule, and it explains the deviations when  $p_c$  is very small or very large when measured in atmospheres. We also have

$$\begin{aligned}\theta_c/\theta_b &= 1 + 1/b \cdot \ln p_c \\ &= 1 + \theta_c/B \cdot \log p_c\end{aligned}$$

For ordinary substances  $p_c$  (in atmospheres) varies from 30 to 60, i.e.  $\log p_c$  varies from 1.48 to 1.78. Putting  $\log p_c = 1.5$  and  $B = 3\theta_c$ , we find  $\theta_b/\theta_c = 2/3$ . But this ratio will be different if  $p_c$  is different from 32 and  $b$  from 7.

If we measure  $p_c$  in millimetres of mercury, since  $\log 760 = 2.88$ , the average value of  $\log p_c$  is about 4.5. Hence, taking  $b = 7$ , we have

$$A = 0.434b + \log p_c = 7.3$$

In the case of metals the critical pressures are much higher and the average value of  $A$  is over 8. The critical elements are rather uncertain. We can certainly take  $b > 3.5$ , so that  $\theta_c < 0.7B$ . And, if  $a$  is the coefficient of volume expansion at low temperatures, we have seen that  $t_c > 0.3/a$ .

Let us see by the case of hydrogen how far we may determine  $p_c$  if  $\theta_c$  is known. The vapour-pressure equation<sup>1</sup> from 14° to 20° abs. is:

$$\log p = 2.501 - 51/\theta$$

where  $p$  is in atmospheres. Here  $B/\theta_c = 1.55$ , since  $\theta_c = 32.2$ , and  $b = 3.56$ . Also

$$\log p_c = A - B/\theta_c = 0.95$$

That is,  $p_c = 8.9$ ; whereas the experimental result is 12.8. Hydrogen is of course exceptional; the agreement is much better in other cases.

An example of equation (16) is that for benzene (Laar, p. 303):  $A = 15.48$ ,  $B = 2275$ ,  $C = 3.54$ , the pressure being in atmospheres. The critical values are  $\theta_c = 561.6$ ,  $p_c = 47.9$  atm. Here  $B/\theta_c = 4$  and  $b = 9.3$ . Also

$$B/\theta_c + \log p_c + C \log \theta_c = 15.47$$

which is practically  $A$ .

If the  $p$ -formula were quite accurate and the law of corresponding states valid, it can easily be shown that

$$2n = (dP/dT)_c = b - c$$

where  $n$  stands for  $r\theta_c/pv_c$ ,  $p$  being in dynes per square centimetre. In the case of benzene just given  $b - c = 5.8$ , whereas  $2n = 7.5$ . But in the case of most substances  $n = 3.67$  and  $b$  in formula (17) = 7.34 is a good approximation. It must be remembered, however, that strictly the formula for  $\log p$  does not hold near the critical point.

Differentiating (16), we have

$$dp/p = d\theta(B - C\theta)/0.434\theta^2 \quad \dots \quad (19a)$$

And from the thermodynamic relation (18a)

$$dp/p = d\theta jw\lambda/r\theta^2$$

<sup>1</sup> Laar, *Die Zustandsgleichung*, 1924, p. 300. If we took the 'theoretical' value of  $A = 2.60$ , we should obtain  $p_c = 11.22$ .

Hence

$$jw\lambda_b r = (B - C\theta)/0.434$$

That is, formula (16) is equivalent to taking  $\lambda$  near the boiling-point as a linear function of the temperature. Integrating (19a) between  $p_b$ ,  $\theta_b$  and  $p$ ,  $\theta$ , we find

$$A = \log p_b + B/\theta_b + C \log \theta_b$$

For normal substances (apart from alcohols and acids), W. H. Banks<sup>1</sup> found the approximate equation

$$\log (w\lambda_b) = 4.31 - 4/w^{\frac{1}{2}}$$

to hold. Putting  $w\lambda_b/\theta_b = 21$ , we find

$$\log \theta_b + 4/w^{\frac{1}{2}} = 2.99$$

If  $\theta_1$  and  $\theta_2$  are the temperatures at which the saturated vapour pressure is the same for two substances 1 and 2, then from (17)

$$B_1/\theta_1 = B_2/\theta_2 + A_1 - A_2$$

Hence the rule of Ramsay-Young: If  $\theta_1/\theta_2$  is plotted against  $\theta_1$ , the curve is a straight line.

If  $\theta_1$ ,  $\theta_1'$  for substance 1 and  $\theta_2$ ,  $\theta_2'$  for substance 2 are temperatures at which the vapour-pressure is  $p$ ,  $p'$ , then

$$\begin{aligned} \frac{\theta_1'}{\theta_1} &= \frac{B_2/\theta_2 + A_1 - A_2}{B_2/\theta_2' + A_1 - A_2} \\ \frac{\theta_1 - \theta_1'}{\theta_2 - \theta_2'} &= \frac{B_1}{B_2} \cdot \frac{(A_2 - \log p)(A_2 - \log p')}{(A_1 - \log p)(A_1 - \log p')} \end{aligned}$$

Hence the rule of Ramsay-Young

$$\theta_1'/\theta_1 = \theta_2'/\theta_2$$

and that of Dühring

$$(\theta_1 - \theta_1')/(\theta_2 - \theta_2') = \text{constant}$$

are true only when  $A_1 = A_2$ .

### Viscosity

Turn to viscosity whose measure-ratio is

$$[\mu] = M/LT = M^{\frac{1}{2}}(G\Theta)^{\frac{1}{2}}V^{-\frac{3}{2}}$$

It follows that

$$\begin{aligned} \mu &= m^{\frac{1}{2}}(g\theta)^{\frac{1}{2}}v_m^{-\frac{1}{2}}\phi \\ &= w^{\frac{1}{2}}v^{-\frac{1}{2}}\theta^{\frac{1}{2}}A\phi \\ &= w^{\frac{1}{2}}v_c^{-\frac{1}{2}}\theta_c^{\frac{1}{2}}AT^{\frac{1}{2}}V^{-\frac{1}{2}}\phi \\ &= w^{\frac{1}{2}}v_c^{-\frac{1}{2}}\theta_c^{\frac{1}{2}}A\psi \end{aligned} \quad (20)$$

where

$$A = g^{\frac{1}{2}}/m_H^{\frac{1}{2}} = 1.3 \times 10^{-4} \text{ and } \psi \equiv T^{\frac{1}{2}}V^{-\frac{1}{2}}$$

At the critical point we have

$$q \quad \mu_c w^{\frac{1}{2}}\theta_c^{-\frac{1}{2}}\theta_c^{-\frac{1}{2}} = 1.3 \times 10^{-4}\psi_c$$

<sup>1</sup> *J. Chem. Soc.*, 1939, 294.

Now  $q$  is found <sup>1</sup> to be about  $3 \times 10^{-5}$ , that is,  $\psi_c$  is about 0.23 and therefore of the order unity.

For a gas the  $V$  which occurs in (20) is taken as referring to the 'molecular volume' or to the co-volume ( $b$ ) of van der Waals. And, assuming ordinary pressures, Sutherland <sup>2</sup> proposed a formula equivalent to taking  $\phi = \text{constant}$  and

$$V^{-\frac{1}{3}} = c/(1 + a/T)$$

Or, otherwise expressed,

$$\psi = cT^{\frac{1}{3}}/(1 + a/T)$$

so that

$$\mu = w^{\frac{1}{3}}v_c^{-\frac{1}{3}}cA\theta^{\frac{1}{3}}/(1 + C/\theta)$$

where  $C = a\theta_c$ . It has been stated <sup>3</sup> that 'Sutherland's formula has been found to be applicable with satisfactory results for all gases'. And Vogel <sup>4</sup> proposed  $C = 1.47\theta_b = 0.98\theta_c$ . But unfortunately many of the values of  $C$  are erroneous owing to experimental error, magnified by extrapolation.<sup>5</sup>

There is much more general evidence, apart from viscosity, for the proposal of Reinganum <sup>6</sup> to use  $\varepsilon^{\frac{a}{T}}$  instead of  $1 + a/T$ . For the co-volume  $b$ , in the case of a gas not too condensed, can be taken as varying with the temperature in accordance with

$$b/b_c = \varepsilon^{\alpha(1/T-1)}$$

where  $\alpha$  is not much different from unity.<sup>7</sup> Taking

$$\mu = KT^{\frac{1}{2}}\varepsilon^{-T}$$

we have

$$\frac{1}{\mu} \frac{d\mu}{dT} = \left(\frac{1}{2} + a\right)/T$$

According to Herz <sup>8</sup> the ratio of  $\mu$  at  $T = \frac{7}{1.2} = 0.583$  to  $\mu$  at  $T = \frac{1}{2} = 0.5$  varies for different substances (apart from alcohols) from 1.9 to 1.6. Taking  $T = \frac{1}{2}$ ,  $dT = \frac{1}{1.2}$ ,  $d\mu/\mu = 0.6$  to 0.9, we find that  $a$  varies from 3.1 to 4.9. But if we use Sutherland's formula

$$\mu = KT^{\frac{1}{2}}/(1 + a/T)$$

$$\frac{1}{\mu} \frac{d\mu}{dT} = \frac{1}{T} \left( \frac{1}{2} + \frac{a}{a+T} \right)$$

we find that  $a$  is negative.

<sup>1</sup> Nasini, *Phil. Mag.*, 1929, 8, 603. A few values of  $q \times 10^{-5}$  are: helium 3.01; hydrogen 2.95; carbon dioxide 2.75; chlorine 2.74; benzene 2.74; acetic acid 2.70; water 3.09.

<sup>2</sup> *Phil. Mag.*, 1893, 36, 511.

<sup>3</sup> Titani, *Bull. Chem. Soc. Japan*, 1930, 5, 106.

<sup>4</sup> *Ann. Physik*, 1914, 43, 1267.

<sup>5</sup> Arnold, *J. Chem. Phys.*, 1933, 1, 170.

<sup>6</sup> *Phys. Zeit.*, 1901, 2, 242; *Ann. Physik*, 1903, 10, 334 and 1904, 28, 142.

<sup>7</sup> Laar, *Die Zustandsgleichung*, 1924, pp. 21, 34, 177. Cf. Schames, *Phys. Zeit.*, 1931, 32, 16.

<sup>8</sup> *Z. anorg. Chemie*, 1922, 123, 132.





$p = 100$ . The explanation lies in the formula, derived from that of van der Waals with external pressure neglected relatively to internal:

$$a/v^2 = r\theta/(v - b)$$

where  $\theta$  varies only from 293 to 313 (T from 0.97 to 1.03). Also the  $p = 100$  is appreciably above the critical (73).

Batchinski's formula can be expressed in the form

$$\mu = K/(V - B)$$

or

$$1/\mu = A'/\rho - B' \quad (22)$$

where  $A' = \rho_c/K$ ,  $B' = A'b/w = A'B/\rho_c$ . It is well known that for pure and mixed liquids and solutions there is a linear relation between the reciprocals of viscosity and density, in accordance with (22). Moreover, the ratio of the coefficients

$$A'/B' = \rho_c/B$$

gives us an estimate of the critical density, which can also be estimated by  $\rho_c = \rho_m/3.120$  where  $\rho_m$  is the density at the melting-point.<sup>1</sup>

Batchinski's formula does not imply that the co-volume  $b$  is not a function of temperature and volume. It only implies what is otherwise known<sup>2</sup> that at temperatures below the boiling point  $b$  is practically constant (= its value at the melting-point). In fact, as Herzog and Kudar<sup>3</sup> have shown, the value of  $b$  required for Batchinski's formula can be calculated quite independently of the viscosity from the well-known formula

$$\frac{\alpha}{\beta} = \frac{r}{v - b} = \frac{r/w}{1/\rho - b/w} \quad (23)$$

applied at the melting-point. Here  $\alpha$  is the coefficient of expansion (at constant pressure) and  $\beta$  the coefficient of elasticity (at constant temperature); and the relation is obtained at once by differentiating van der Waals's equation. Thus:

	$b/w$ from (22) = $B'/A'$	$b/w$ from (23)	$B = b\rho_c/w$ from (23)
Benzene . . . . .	1.0476	1.045	0.318
Ethyl ether . . . . .	1.546	1.155	0.302
Bromine . . . . .	0.288	0.285	0.34

Another formula<sup>4</sup> for the viscosity of liquids is

$$\mu = ae^{b/\theta}$$

or

$$\log \mu = -A + B/\theta$$

Here, except for water and alcohols,  $b$  is very approximately  $jw\lambda_m/r$ .

<sup>1</sup> Aubel, *Ac. R. de Belgique Bull. (Classe des Sciences)*, 1926, 13, 277.

<sup>2</sup> Laar, *Die Zustandsgleichung*, 1924, p. 86.

<sup>3</sup> Z. f. Phys., 1933, 80, 222.

<sup>4</sup> Guzman, *Anales de la Soc. Espan. de Fisica y Quimica*, 1913, 11, 353; Dunn, *Trans. Far. Soc.*, 1926, 22, 401; Kenkatarama Iyer, *Ind. J. Phys.*, 1930, 5, 371; Prasad, *Phil. Mag.*, 1933, 16, 263; Waller, *ibid.*, 1934, 18, 505; Herzog and Kudar, *Z. f. Phys.*, 1933, 80, 230. The formula is improved by putting  $\theta - \theta_0$  for  $\theta$ —Tonomura, *Sci. Rep. Tohoku*, 1933, 22, 123.

*Molecular Refraction*<sup>1</sup>

If  $\epsilon$  is the (electrostatic) dielectric constant, or  $\epsilon = n^2$  the square of the index of refraction for long waves in a transparent medium, then according to the Clausius-Mossotti theory of dielectrics,

$$R \equiv v(\epsilon - 1)/(\epsilon + 2)$$

is equal to  $u$ , 'the real volume occupied by the molecules' in 1 mol. It is found that  $R$  is very approximately independent of temperature, pressure and changes in the state of aggregation. It is not easy to assign a clear meaning to the volume  $u$ . But we can put

$$u/v_c = \phi(V, T)$$

Experiment shows that  $\phi$  is constant, say,  $1/f$ . Hence

$$R = v_c/f$$

It is found<sup>2</sup> that for ordinary substances such as benzene, ether, carbon tetrachloride, toluene,  $f$  is about 10. Also  $r\theta_c/p_c v_c$  is about 3.7, where  $p_c$  is in dynes per square centimetre  $= 1.014 \times 10^6 q_c$ , if  $q_c$  is in atmospheres. Hence we obtain Guye's formula

$$R = 2.3 \theta_c/q_c$$

Davies also verified that

$$(\epsilon + 2)/(\epsilon - 1)2\alpha\theta_c = 2.5$$

Or, using (10c),

$$R = v_0/2.5 = v_c/10$$

We find that very approximately for the D line of sodium  $n_c = 1.126$ . Hence

$$R/v_c = (n_c^2 - 1)/(n_c^2 + 1) = 1/12$$

Regarding the molecules (N per mol) as hard elastic spheres (of diameter  $d$ ), we may put  $u = \pi N d^3/6$ . It can be shown<sup>3</sup> by elementary reasoning—whose validity is not irreproachable—that we can allow for the finite size of the molecules by replacing  $v$  in the equation  $p v = r\theta$  by  $v - b$ , where

$$b = 2\pi N d^3/3 = 4u$$

Taking  $u = v_c/10$ , this gives  $b = 0.4 v_c$ , and taking  $u = v_c/12$ , we find  $b = 0.3 v_c$ . Thus we reach once more the value of the co-volume which occurs in Batchinski's formula for the viscosity of a liquid. But, as we have already seen, there is reason to believe that for a gas we must take

$$b = b_c \epsilon^{\frac{1}{T}-1} \\ = b_c/\epsilon(1 + 1/T + \dots)$$

Applying the same formula to  $u$ , we have

$$R = A + B/\theta$$

This has been verified in modern refined experiments. It is curious to find

<sup>1</sup> See Vol. II, p. 503.

<sup>2</sup> Traube, *Ann. Physik*, 1901, 5, 552; Davies, *Phil. Mag.*, 1912, 24, 417. For pentane  $f$  is about 12, for methyl acetate and acetic acid about 13.

<sup>3</sup> Jeans, *Dynamical Theory of Gases*, 1916<sup>2</sup>, pp. 139, 172.

these simple and apparently antiquated ideas leading to the results of modern polarization theories.<sup>1</sup>

### *The Melting-Point*

If  $\theta_m$  is the melting-point and  $\lambda_m$  the latent heat of fusion, we should expect  $w\lambda_m/\theta_m$  to be approximately constant on the supposition that  $T_m$  is constant. Taking  $T_m$  on the average to be 0.44, we find from (14) and (14a)

$$w\lambda_m/\theta_m = 10.8$$

This is approximately true and the approximation can of course be improved by adjusting the constant A. But differences due to chemical composition begin to be noticeable.<sup>2</sup> If we make bold to extrapolate our method to solids, using  $w$  to denote the *atomic* weight, we might expect  $w\lambda_m/\theta_m$  to be constant. And in fact the value is about 2.6 (but 1.7 for the alkali metals).

An equation similar to (17)

$$\log p = A' - B'/\theta$$

holds for the vapour-pressure of solid metals. J. Richards<sup>3</sup> assumes that, if  $\lambda_1 = \lambda_m + \lambda_b$  is the latent heat of sublimation, and  $w\lambda_m/\theta_m = 2.1$ ,

$$\begin{aligned} B' &= 0.22w\lambda_1 \\ &= B + 0.22w\lambda_m \\ &= B + 0.46\theta_m \end{aligned}$$

At the melting-point the vapour pressure of the solid is equal to that of the liquid. That is,

$$A - B/\theta_m = A' - B'/\theta_m$$

Hence

$$A' = A + 0.46$$

De Forcrand,<sup>4</sup> extending a result of Le Chatelier, proposed the formula

$$w(\lambda_m + \lambda_b)/\theta_b = wq/\theta_1 = 30$$

Here  $wq$  is the heat of dissociation per mol; when the substance, combined with a solid body, is progressively heated its dissociation pressure increases until it reaches atmospheric pressure at the temperature  $\theta_1$ . Since by Trouton's rule  $w\lambda_b/\theta_b = 21$ , this implies  $w\lambda_m/\theta_b = 9$ . If we take  $\theta_b/\theta_m = 4/3$ , this gives  $w\lambda_m/\theta_m = 12$ .

<sup>1</sup> Smyth, *Dielectric Constant and Molecular Structure*, 1931, p. 19.

<sup>2</sup> Mortimer, *J. Amer. Chem. Soc.*, 1922, 44, 1433: aromatic hydrocarbons 12.8; halogen compounds 13.5; nitro compounds 13.5; amino compounds 11.0; aromatic hydroxy compounds 6.9; aromatic acids, anhydrides and ketones 12.1. According to Parks and Todd, *Ind. Eng. Chem.*, 1929, 21, 1235, for normal paraffin hydrocarbons

$$w\lambda_m/\theta_m = 4n^{0.836} - 1.43,$$

where  $n$  is the number of carbon atoms in the molecule.

<sup>3</sup> Richards, *J. Franklin Inst.*, 1919, 187, 588. For mercury:  $A' - A = 0.49$ ,  $B' - B = 0.46 \times 239$ .—Poindexter, *Phys. Rev.*, 1925, 26, 859. The m.p. of mercury is 234.2° (Abs.).

<sup>4</sup> *Ann. Chim. Phys.*, 1903, 28, 416.

*Solid Elements*

Let us tentatively apply this method to solid elements, i.e. we take  $w$  to be the atomic weight and regard the elements as having 'atomic similarity'. Sometimes we obtain surprisingly good results. And we invariably obtain the right order of magnitude. This last follows from the fact that we are using the principle of tautometric products. Our assumptions are: (1) If  $H$  is the measure-ratio of heat,  $JH = K\Theta = ML^2/T^2$ , which strictly only holds for a gas. (2) Instead of using a tautometric function  $p_1 = \phi(p_2)$ , we take  $p_1 = Cp_2$  as approximately true at ordinary temperatures.

(a) Rule of Dulong and Petit:  $wc = \text{constant}$ , where  $c$  is the specific heat. Now

$$[mc] = H/\Theta = K/J$$

Hence

$$wc = Ak/jm_H = Ar/j = 2A$$

In fact,  $wc$  is about 6.4, with well-known exceptions and with failure at low temperatures.<sup>1</sup>

(b) According to Grüneisen,<sup>2</sup> if  $a$  is the coefficient of linear expansion of a metal ( $al_0 = dl/d\theta$ ) and  $c$  the specific heat at constant pressure,  $a/c$  is independent of the temperature. As a matter of fact,  $a/c$  slowly increases with temperature. A better result is obtained from  $\alpha/c$ , which (see p. 114) is equal to  $\alpha(1 - \alpha t)/c$  and is appreciably more constant. The formula makes no attempt to connect the constants of the different metals. The measure-ratio of  $\alpha/c$  is  $M/H$ . But that of  $\lambda_m\alpha/c$  is  $J/K$  and we find the quantity to be approximately constant ( $7.5 \times 10^{-3}$ ) for different metals.<sup>3</sup> L  meray<sup>4</sup> pointed out that  $\alpha\theta_m$  is about 0.02 for metals, and Wiebe<sup>5</sup> showed that  $w\alpha\theta_m$  is about 0.13.

(c) According to Einstein,<sup>6</sup>  $v/\beta\theta_m$  is constant for different metals, where  $\beta$  is the compressibility (inverse of bulk modulus). Now

$$[m\alpha/\rho\beta] = K$$

hence

$$v\alpha/\beta = Ar = A \times 8.3 \times 10^7$$

The value lies between 15 and  $20 \times 10^7$ , i.e.  $A$  is of the order unity. Compare formula (23) above.

(d) The analysis (initiated by Debye) of specific heat phenomena in solids presupposes a connection between the interatomic forces determining elasticity and those concerned in infra-red frequencies. That is, the characteristic frequency  $n$  is a function of  $\beta$  (the compressibility),  $m$  and  $v_m$  (the atomic mass and volume). Now  $N = 1/T$  and  $[\beta] = LT^2/M$ , so that

$$N = L^{\frac{1}{2}}[\beta^{-\frac{1}{2}}]/M^{\frac{1}{2}}$$

<sup>1</sup> According to the quantum theory:  $wc_v = 5.96f(x)$  where  $x \equiv hn/k\theta$  is a new tautometric product. This function becomes important only at low temperatures.

<sup>2</sup> *Ann. Physik.*, 1908, 26, 211.

<sup>3</sup> Schiller, *Z. f. Phys.*, 1921, 5, 161. Also  $w\lambda\alpha$  is approx. constant for the elements, about unity (0.82 for zinc and 1.6 for tin).—Doi, *Sci. Pap. Tokyo*, 1927, 6, 143.

<sup>4</sup> *Compt. rend.* (Paris), 1900, 131, 1291.

<sup>5</sup> *Ann. Physik.*, 1906, 19, 1076. This also follows by combining L  meray with Dulong and Petit.

<sup>6</sup> *Ann. Physik.*, 1911, 35, 690.

Hence

$$\begin{aligned} n &= C v_m^{\frac{1}{3}} \beta^{-\frac{1}{3}} m^{-\frac{1}{3}} \\ &= C m_H^{-\frac{1}{3}} w^{-\frac{1}{3}} \rho^{-\frac{1}{3}} \beta^{-\frac{1}{3}} \end{aligned}$$

and  $m_H^{-\frac{1}{3}} = 8.6 \times 10^7$ . Experiment gives

$$n = 3.3 \times 10^7 / w^{\frac{1}{3}} \rho^{\frac{1}{3}} \beta^{\frac{1}{3}}$$

This formula was first reached by Einstein<sup>1</sup> from such general considerations, and then deduced theoretically by Debye. As a matter of fact, this formula also gives the greatest frequency of the infra-red absorption bands of a liquid; in this case we must revert to our former notation;  $w =$  molecular weight.

We can similarly arrive at Lindemann's formula<sup>2</sup>

$$n = (A \times 7.6 \times 10^{11}) \theta_m^{\frac{1}{3}} / w^{\frac{1}{3}} v^{\frac{1}{3}}$$

According to experiment the coefficient is  $31 \times 10^{11}$ , so that  $A$  is of the order unity. Another formula<sup>3</sup> is

$$\nu = (C \times 7 \times 10^{11}) c^{\frac{1}{3}} / \alpha^{\frac{1}{3}} v^{\frac{1}{3}}$$

in which (if  $\alpha$  is taken as the cubic coefficient) experiment gives  $2.9 \times 10^{11}$  as the value of the bracketed factor.

(e) Suppose the heat-conductivity ( $k$ ) is a function of atomic (or molecular) mass ( $m$ ), atomic (or molecular) volume ( $v_m$ ), characteristic infra-red frequency ( $n$ ) and temperature ( $\theta$ ). The measure-ratio of  $k$  is

$$[k] = H/LT\Theta = ML/JT^3\Theta$$

Hence

$$\begin{aligned} jk &= C m v_m^{\frac{1}{3}} n^3 / \theta \\ &= C \times m_H^{\frac{1}{3}} w v^{\frac{1}{3}} n^3 / \theta \\ &= (C \times 1.97 \times 10^{-32}) w v^{\frac{1}{3}} n^3 / \theta \end{aligned}$$

in ergs per cm. per sec. per degree. Thus the conductivity is inversely proportional to the absolute temperature, as is well known.<sup>4</sup> Also if we apply the equation to the alkali halides, for example, i.e. taking  $w$  to be the molecular weight, the factor in brackets is found to be  $1.5 \times 10^{-32}$ .

(f) If  $s$  is surface-tension, we have, just as in the case of ordinary liquids,

$$s v^{\frac{2}{3}} / \theta = C$$

If we evaluate this, at the melting-point, for non-metallic elements for which the quantities are known, we find that  $C$  varies between 0.96 and 1.25; for hydrogen it is 0.77 and for nitrogen 0.80.

(g) The measure-ratio of  $c/\alpha$  is

$$H/M = L^2/JT^2 = U^2/J$$

<sup>1</sup> *Ann. Physik*, 1911, 35, 686. Debye subsequently gave a theoretical formula containing  $7.4 \times 10^7 f(\sigma)$ , where  $\sigma$  is Poisson's constant, instead of  $3.3 \times 10^7$ .—*Ibid.*, 1912, 39, 816. Cf. Gapon, *Z. f. Phys.*, 1927, 44, 600.

<sup>2</sup> *Phys. Zeit.*, 1910, II, 609. The numerical factor represents  $k^{\frac{1}{3}}/m_H^{\frac{1}{3}}$ . By  $v$  is meant the atomic volume ( $w/\rho$ ).

<sup>3</sup> Cf. Grüneisen, *Ann. Physik.*, 1912, 39, 291. The numerical factor is  $j^{\frac{1}{3}}/m_H^{\frac{1}{3}}$ .

<sup>4</sup> At low temperatures (but not in the region of superconductivity):  $k/wc = a/\theta + b$ , where  $a$  and  $b$  are constants for each metal.—Bidwell, *Phys. Rev.*, 1928, 32, 311.

Hence we may conjecture a relation between the velocity of sound ( $u$ ) and  $j^{\frac{1}{3}}(c/\alpha)^{\frac{1}{3}}$ . Kleiber<sup>1</sup> gave the formula, applicable to metals,

$$u = Cj^{\frac{1}{3}}(c/\alpha)^{\frac{1}{3}} - 63700$$

where  $u$  is in cm./sec. and  $C = 0.892$ .

It will thus be seen that by elementary metrical considerations, without entering into theoretical details, we can see the way in which quantities are grouped as well as the order of magnitude involved.

<sup>1</sup> *Ann. Physik*, 1915, 46, 1054.

## CHAPTER IV

### OBSERVATIONS AND CALCULATIONS <sup>1</sup>

#### SECTION 1: ERRORS OF OBSERVATION

**I**NTRODUCTION. Before commencing a series of experiments a preliminary investigation should always be carried out so as to decide in what manner the work must be planned in order to attain the desired degree of accuracy.

The first point to be considered is the exactness with which the quantity to be measured is defined. For example, we may determine the specific gravity of copper on one occasion and that of the same, or another sample of the same metal, on another: however carefully we proceed the results obtained will not be exactly equal; the amount of this disagreement is what we mean by the lack of definition of the quantity. The accuracy of the measurements we make must therefore correspond with the exactness of definition of the object to be measured, and no advantage will be secured by exceeding this degree of accuracy. Thus, if we regard the degree of accuracy of ordinary volumetric work as not exceeding 1 part in 1,000, and we wish to make up a litre of normal oxalic acid, no useful purpose will be served by weighing out 63 grams of the crystals with a greater accuracy than to the second decimal place. It is advisable that weighings should be of an order one degree higher than the accuracy of the titration to avoid the chance of doubling the error.

**Errors.** The errors which may affect the accuracy of a result may be classified as constant, systematic, and accidental errors.

**Constant Errors.** By the term constant error we mean some factor the existence of which has not been recognized and which affects the accuracy of the result in one direction—it has the same magnitude and sign and has the same effect upon all the observations of a series. Perhaps one of the best examples of a constant error is that which has led to the discovery of argon. The density of nitrogen from atmospheric air was redetermined by Lord Rayleigh in 1893, the value obtained being 1.25718 grams per litre at N.T.P., in very good agreement with results of previous determinations. The remedy we have against the results of constant errors lies in varying the conditions of the experiment to as great an extent as possible, obtaining starting materials from as widely differing sources as possible, purifying and separating the material by different processes, and making the final determinations by different methods. In

<sup>1</sup> The section on Errors and Observations in the 2nd ed. has been revised and re-written in greater part by Dr. M. D. McCarthy, University College, Cork. He has also written Section 4 in this chapter on Graphical Methods.



Rayleigh's case it was found that when the nitrogen was obtained from a source other than the atmospheric air, namely, ammonia, the density obtained differed by 1 part in 200 from that previously obtained. This difference was later shown by Rayleigh and Ramsay to be due to the fact that a constant error had been present in all the earlier determinations—the nitrogen used had always been obtained from atmospheric air, and this nitrogen always contains more than 1 per cent of the heavier gas argon, till then unknown.

**Systematic Errors** have a sign and magnitude which bear a fixed relation to one or more of the conditions of observation. The disagreement between individual observations in a series is due to errors of observation. Observations may be affected by the instrument used, the external conditions at the time of observation, and the observer.

Instrumental errors may be caused by errors of graduation of a scale or by lack of adjustment of the instrument. The presence of these errors must be sought out carefully so that their effects can be eliminated. Scales, weights, thermometers, and so forth must be calibrated, instruments must be tested for lack of accurate adjustment. In some cases it is possible to arrange the system of observations so that the instrumental errors balance out: thus the effect of the inequality of the arms of a balance may be overcome by weighing the object in both pans of the balance.

External conditions may affect the observations and be out of the control of the observer; in this class we have such factors as the variation of the room temperature or the barometric height. Rapid fluctuations of such conditions are particularly troublesome: allowances can sometimes be made for regular variations, but in the case of violent fluctuations it is often necessary to suspend work until stable conditions can be secured.

Another class of error is the personal error—an inexperienced observer will commit errors in his observations of varying magnitude and sign, while a careful observer, well experienced in the particular determination he is carrying out, is often found to commit an error which is of the same sign and approximately of the same magnitude—this is referred to as the personal equation of the observer. It should be particularly noted that only a careful experienced worker is likely to have a well-defined personal equation, and then only when in his normal state (of health or freedom from fatigue). The personal error can be determined by checking against fixed standards and can then be allowed for.

**Accidental Errors.** Were it possible to secure freedom from all constant and systematic errors, variations would still be found in a series of observations. These are due to accidental errors. Accidental errors, then, are those whose causes and laws of action are unknown.

Strictly speaking, any observation is affected by the state of the whole universe at the moment of observation, and a later observation will be influenced by all changes which have taken place in the universe in the interval. It is impracticable for an observer to note the condition of the whole universe at the time he makes his observation; he has therefore to content himself with selecting those factors which in his opinion will materially affect the observation. He confines his attention to the essential conditions as far as he is able to judge what these conditions are; but owing

to the incomplete state of his knowledge, his judgment as to what are the essential conditions may be at fault, and in any case those other conditions which have too small an effect to justify their selection among the essential conditions will still produce their effects, however small, and the sum of these will be the accidental error. Among these accidental errors will be included those due to changes in the personal error of the observer and those residual instrumental errors which have either escaped detection or which have not been exactly corrected for: similarly an error due to a reading being wrongly recorded would be included—we say it is due to carelessness, but in reality we do not know the reason.

Now when the plan of experiment has been decided upon with the idea of avoiding or correcting for constant and systematic errors, we know that accidental errors will still remain, and it becomes our business to determine what is the most probable value of the quantity we are trying to determine. The final series of observations made with all possible care and corrected for all known sources of error may be referred to as the observed values, and in what follows will be supposed to be free from constant and systematic errors.

**Normal Law of Error.** Suppose that the 'true value' of the quantity which is being observed is  $\mu$ , and that the observations are subject only to accidental errors which satisfy the following conditions:

1. The total error is made up of a large number of independent accidental errors, the total error being the algebraic sum, or at any rate a linear function, of these partial errors.
2. The 'expected' value of each partial error is zero.
3. That certain general conditions regarding the probability laws of the partial errors hold; that, for instance, the second and third absolute moments of these partial errors are bounded.

It may then be shown that<sup>1</sup> the probability that an observation will lie between  $x - \frac{1}{2}dx$  and  $x + \frac{1}{2}dx$ ,  $dx$  being an infinitesimal, is

$$(2\pi\sigma^2)^{-\frac{1}{2}} \exp\left\{-\frac{1}{2}(x - \mu)^2/\sigma^2\right\} \cdot dx \quad . \quad . \quad . \quad (1)$$

The probability that an observation will lie in some finite interval, say between  $a$  and  $b$  ( $a < b$ ), is

$$(2\pi\sigma^2)^{-\frac{1}{2}} \int_a^b \exp\left\{-\frac{1}{2}(x - \mu)^2/\sigma^2\right\} \cdot dx \quad . \quad . \quad . \quad (2)$$

This probability law is usually known as the Normal Law or the Law of Gauss (though it was known earlier to De Moivre). The strict validity of treating experimental errors in terms of the normal probability law, that is the validity of the hypotheses made about the accidental errors, is open to question. An objection of general appeal is that the possible range of observations under the normal law is from  $+\infty$  to  $-\infty$ , while in the case of practically all physical measurements such a position is inconceivable. The normal law does, however, occupy the most important position among error laws and in fact it is a not unusual procedure, when the measurements with which we deal are not normally distributed, to deal instead with some function of them, e.g.  $\sqrt{x}$  or  $\log x$ , which does, approximately at any rate,

<sup>1</sup> See, for instance, Levy, *Calcul de Probabilités* (Gauthier-Villars). Bernstein, *Math. Annalen*, 1927, 97, 1-59. Kozakiewicz, *Ann. de la Soc. Polonaise de Math.*, 1934, 13, 24-43.

obey this law. We shall assume, in what follows, that the normal law holds for the errors with which we have to deal.

Fig. 1 (IV) represents a graph of the function

$$y = (2\pi\sigma^2)^{-\frac{1}{2}} \exp\left\{-\frac{1}{2}(x - \mu)^2/\sigma^2\right\} \quad . \quad . \quad . \quad (3)$$

This curve is symmetrical about its maximum ordinate  $y_0 = (2\pi\sigma^2)^{-\frac{1}{2}}$  which occurs when  $x = \mu$ . As  $|x - \mu|/\sigma$  increases, the value of  $y$  falls off symmetrically, the decrease being rapid until this fraction is about 3, whence the curve becomes asymptotic to the  $x$  axis. The total area between the curve and the  $x$  axis is unity, while the area, which is shaded in Fig. 1(IV), between the curve, the  $x$  axis and the ordinates  $x = a$  and  $x = b$  represents the prob-

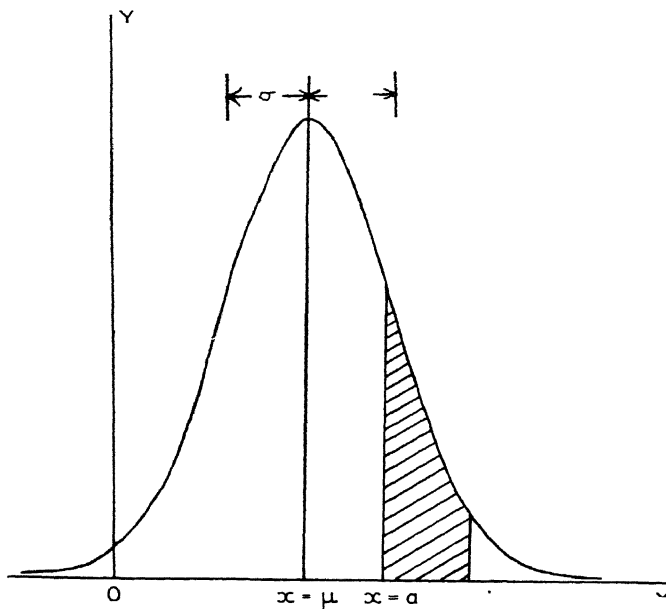


FIG. 1 (IV)

ability that an observation will lie in the interval  $(a, b)$ , where  $a < b$ , when the normal error law (1) applies.

The two quantities  $\mu$  and  $\sigma$  which occur in these equations are known as *parameters*.  $\mu$  obviously determines where the maximum ordinate of the curve is situated, while  $\sigma$  measures the 'spread' of the curve about this ordinate.  $\mu$  is the 'true value' of the quantity being measured and is called the 'theoretical (or population) mean'.  $\sigma^2$  is known as the 'theoretical variance', while  $\sigma$  is the 'theoretical standard error' or 'standard deviation'. Sometimes certain functions of  $\sigma$  are used in its stead, e.g. the 'modulus of precision',  $h = (2\sigma^2)^{-\frac{1}{2}}$ , or the so-called 'probable error', which is  $0.6745\sigma$ . The widespread use of this last quantity is its only recommendation.

The terms 'theoretical' or 'population' are used to distinguish these hypothetical, and except on an infinite number of observations, inaccessible quantities  $\mu$  and  $\sigma$  from estimates of them made from a limited number of observations. We shall use Greek symbols for the theoretical 'true values' and Roman letters to denote estimates of them made from the observations.

It may be noted that

$$(a) \text{ Theoretical Mean } (\mu) = (2\pi\sigma^2)^{-\frac{1}{2}} \int_{-\infty}^{\infty} x \exp\{-\frac{1}{2}(x - \mu)^2/\sigma^2\} \cdot dx$$

$$(b) \text{ Theoretical Variance } (\sigma^2)$$

$$= (2\pi\sigma^2)^{-\frac{1}{2}} \int_{-\infty}^{\infty} (x - \mu)^2 \exp\{-\frac{1}{2}(x - \mu)^2/\sigma^2\} \cdot dx$$

If  $n$  independent observations are made, each of which follows the error law (1), and if the number  $m$  of these which lie in the interval  $(a, b)$  is

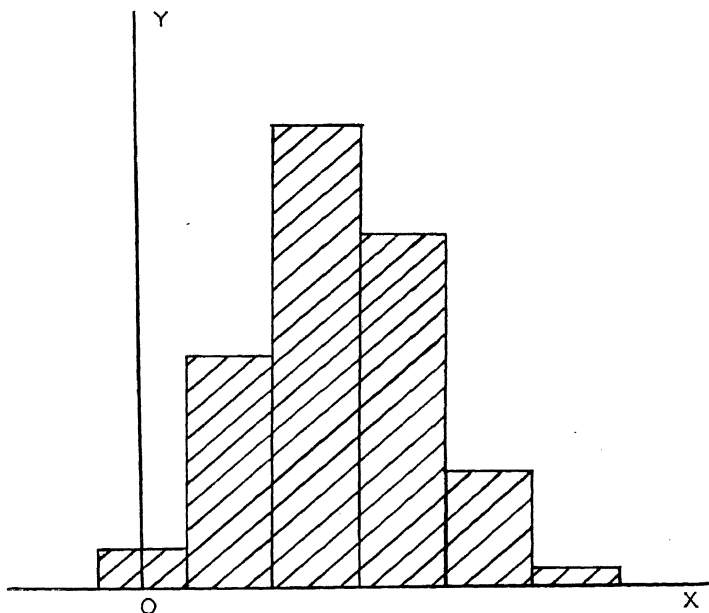


FIG. 2 (IV)

obtained, it will be found that as  $n$  increases the ratio  $m/n$  tends to become equal to the shaded area in Fig. 1 (IV), or to the corresponding integral (2). If the range of these  $n$  observations be divided into, say,  $k$  equal intervals, the proportion of the total number falling into each of these intervals may be found. Taking each interval as the base of a rectangle, and making the area of each rectangle equal to the proportion of the observations falling in the interval, a diagram such as Fig. 2 (IV) will be obtained. Diagrams of this type are called 'histograms'. If  $n$  and  $k$  increase, while the width of

each interval decreases, the discontinuous steps of the histogram in Fig. 2 (IV) tend to the continuous curve of Fig. 1 (IV).

If  $x$  be one observed value of the magnitude whose 'true value' is  $\mu$ , then  $z = x - \mu$  is the 'true error' of the observation  $x$ . If the observations are normally distributed round  $\mu$ , as in (1), then it may readily be seen that the probability that  $z$  lies in the infinitesimal interval  $z \pm \frac{1}{2}dz$  is

$$(2\pi\sigma^2)^{-\frac{1}{2}} \exp\{-\frac{1}{2}z^2/\sigma^2\} \cdot dz$$

and, from this, it readily follows that the probability that the error lies between  $\pm k\sigma$  [i.e. the probability that  $x$  lies between  $\mu \pm k\sigma$ ] is  $p$ , where

$$\begin{aligned} p &= (2\pi\sigma^2)^{-\frac{1}{2}} \int_{-k\sigma}^{+k\sigma} \exp(-z^2/2\sigma^2) \cdot dz \\ &= (2\pi)^{-\frac{1}{2}} \int_{-k}^{+k} \exp(-\frac{1}{2}t^2) \cdot dt \\ &= 2(2\pi)^{-\frac{1}{2}} \int_0^k \exp(-\frac{1}{2}t^2) \cdot dt \end{aligned}$$

Obviously the probability that the error is greater in absolute magnitude than  $k\sigma$  is  $1 - p$ , which may be expressed in the form

$$1 - p = 2(2\pi)^{-\frac{1}{2}} \int_k^\infty \exp(-\frac{1}{2}t^2) \cdot dt$$

Tables of this integral are well known<sup>1</sup> and they make it possible to find  $k$  for a given  $p$  or *vice versa*. Table I gives a brief summary of certain corresponding values of  $p$  and  $k$ .

TABLE I

$p$	0.00	0.25	0.50	0.75	0.95	0.99	1.00
$k$	0.00	0.32	0.67	1.15	1.96	2.58	$\infty$

We may, therefore, say that the probability of getting an observation within the range  $\pm 0.6745\sigma$  on either side of the 'true value' is 0.5, or that, in a long series of observations which are normally distributed, about 50 per cent will be within the range  $\mu \pm 0.6745\sigma$ . Similarly we may see that a range of  $\pm 3\sigma$  on either side of  $\mu$  will in the long run contain about 99.7 per cent of the observations and that the theoretically unlimited range of the normal law is not such a serious drawback as would at first sight appear. It is also evident from the definition of the 'probable error' that the range 'true value'  $\pm$  'probable error' is that range which contains one-half the observations.

In trying to estimate  $\mu$  it is reasonable to prefer those observations which obey an error law with the least possible 'spread'. It is desirable for greater accuracy that a given range on either side of the 'true value' contains as

<sup>1</sup> Pearson, *Tables for Statisticians and Biometricians* (Part I) (Univ. Coll., London); Fisher, *Statistical Methods for Research Workers* (Oliver and Boyd); Brunt, *Combination of Observations* (Camb. Univ. Press); Yates, *Statistical Tables for Biological, Agricultural and Medical Research* (Oliver and Boyd).

great a proportion of a long series of observations as possible. Since, the error law being normal, the proportion of the observations to be expected in the range  $\mu \pm k\sigma$  depends only on  $k$ , it is desirable that the standard error of the observations should be as small as possible. At any rate, the size of  $\sigma$ , with a table of the normal integral, will give an idea of the accuracy of the estimate in question, and therefore it is well to make an estimate of  $\sigma$  as well as of  $\mu$ , from whatever observations are available.

One point should be noted about all the probability statements made above, i.e. that they apply only to the chance of obtaining observations in certain intervals when the 'true values' of  $\mu$  and  $\sigma$  are known. It is not possible to make similar statements as to the probability of the parameters lying in given intervals when a series of observations are known. It is, however, possible to show how to make valid estimates of these parameters and how to assign an interval of which it can be said, with a measurable degree of confidence, that it contains the 'true value' of  $\mu$ .

**Estimation of the Parameters.** A series of observations are made and these are assumed to obey an error law of the type (1). The problem, then, is to obtain from these observations the 'best' possible estimates of the theoretical parameters  $\mu$  and  $\sigma$ .

Let  $x_1, x_2, x_3, \dots, x_n$  be a series of  $n$  such observations. The *arithmetic mean* of these  $n$  quantities is written as  $\bar{x}$ , where

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i = \frac{1}{n} (x_1 + x_2 + x_3 + \dots + x_n)$$

A very important property of the arithmetic mean is that if  $x_1, x_2, x_3, \dots, x_n$  are independent quantities, such that each of them follows the error law (1), then  $\bar{x}$  is distributed normally round the same 'true value',  $\mu$ , as each of the  $x$ 's, but its standard error is  $\sigma/n^{1/2}$ . Obviously, as  $n$  increases, the standard error of the arithmetic mean decreases and this suggests it as a suitable 'statistic' or estimate for  $\mu$ .

If  $\mu$  is known the best estimate to take for  $\sigma^2$  is  $\frac{1}{n} \sum_{i=1}^n (x_i - \mu)^2$ ; but usually  $\mu$  is unknown. In that case it is necessary to substitute  $\bar{x}$  for  $\mu$  and this introduces a bias into the estimate for which the necessary adjustment may be made by writing  $n - 1$  for  $n$  in the above formula. Consequently the estimate adopted for  $\sigma^2$  is  $s^2$ , where

$$s^2 = \frac{1}{n - 1} \sum_{i=1}^n (x_i - \bar{x})^2$$

The bias in taking  $\sum_{i=1}^n (x_i - \bar{x})^2/n$  for  $s^2$  instead of the expression given is, of course, small except when  $n$  is small.

A number of other 'statistics' have been suggested for  $\mu$  and  $\sigma$ . For instance, the *median* of the  $n$  observations might be taken as an estimate of  $\mu$ . The *median* is defined to be the  $m + 1$ th observation, when  $n = 2m + 1$ , and to be one-half the sum of the  $m$ th and the  $m + 1$ th when  $n = 2m$  and the observations are ranged in order of magnitude. Ease of calculation may make it desirable to choose the median instead of the arithmetic mean as the estimate of  $\mu$  to be used. The loss in so doing may be judged from

the fact that, when calculated from a large number of observations, the mean and median both vary normally round  $\mu$ , but the standard error of the mean is  $\sigma/n^{1/2}$ , while that of the median is  $\pi^{1/2}\sigma/(2n)^{1/2}$ , i.e. the standard error of the median is 1.253 times that of the mean in a large sample of observations. A possible estimate of  $\sigma$  might be based on the mean deviation, that is the mean of the quantities  $x_1 - \bar{x}, x_2 - \bar{x}, \dots, x_n - \bar{x}$  where the positive value of each difference, or 'residual', is taken. The estimate which is usually taken is  $s'$ , where

$$s' = \frac{\pi}{(2n(n-1))^{1/2}} \sum_{t=1}^n |x_t - \bar{x}|$$

However, it may be shown that the 'best' estimates to take for  $\mu$  and  $\sigma$  are  $\bar{x}$  and  $s$  as already defined. These quantities constitute what is called a 'sufficient set of statistics' for  $\mu$  and  $\sigma^2$ , and, assuming normality, they 'convey the whole of the information, which the sample of observations contains, respecting the values of the parameters'.

**Calculation of  $\bar{X}$  and  $S$ .** The slowest way to calculate these quantities is to evaluate them directly from their definitions. It is possible, for instance, to add all the observations, total  $S_1$ , divide by the number of observations  $n$ , and so obtain  $\bar{x}$ . This quantity  $\bar{x}$  might then be subtracted from each observation, the 'residual' squared, the squares added, and the total divided by  $n - 1$ , thus giving  $s^2$ . A somewhat better method is to note that

$$\begin{aligned} \sum_{t=1}^n (x_t - \bar{x})^2 &= \sum_{t=1}^n x_t^2 - 2\bar{x} \sum_{t=1}^n x_t + n\bar{x}^2 \\ &= \sum_{t=1}^n x_t^2 - n\bar{x}^2 \\ &= \sum_{t=1}^n x_t^2 - \left( \sum_{t=1}^n x_t \right)^2 / n \end{aligned}$$

That is,  $\bar{x}$  is obtained by adding all the observations, as before, and dividing by  $n$ . The observations are all squared and the squares added the total being  $S_2$ , say. Then  $s^2$  is obtained from the formula

$$s^2 = \frac{1}{n-1} [S_2 - S_1^2/n]$$

As a general rule a still better method is to take an arbitrary origin, say  $a$ , somewhere near where the mean may be expected to lie and to work in terms of deviations from  $a$ . Putting  $y_t = x_t - a$ , or  $x_t = y_t + a$ ,

$$\begin{aligned} \bar{X} &= \frac{1}{n} \sum_{t=1}^n x_t = \frac{1}{n} \sum_{t=1}^n (y_t + a) \\ &= \frac{1}{n} \sum_{t=1}^n y_t + a \\ &= \bar{y} + a \end{aligned}$$

<sup>1</sup> See, for example, Fisher, *Phil. Trans.*, 1922, 222A, 309; Fisher, *Proc. Camb. Phil. Soc.*, 1925, 22, 700-25; Fisher, *Proc. Roy. Soc.*, 1934, 144A, 285-307; Neyman, *Giornale dell' Inst. Ital. degli Attuari*, 1935, 6, 320; Neyman and Pearson, *Stat. Research Memoirs*, 1936, 1, 113-37.

while

$$\begin{aligned}\sum_{t=1}^n (x_t - \bar{x})^2 &= \sum_{t=1}^n [y_t - a - (\bar{y} - a)]^2 \\ &= \sum_{t=1}^n (y_t - \bar{y})^2 \\ &= S_2' - (S_1')^2/n\end{aligned}$$

where now  $S_1'$  and  $S_2'$  stand for the sum of the quantities  $y_t = (x_t - a)$  and of their squares, respectively. The application of this method to a series of fifteen observations, given by Rudberg, of the coefficient of expansion of dry air is given in Table II. The arbitrary origin is taken at  $3,650 \times 10^{-6}$ , and the factor  $10^{-6}$  is omitted in the work.

TABLE II

No. of expt.	Observed value ( $x_t$ )	Dev. from arb. origin ( $y_t = x_t - a$ )	Deviation squared ( $y_t^2$ )
1	3,643	- 7	49
2	3,654	4	16
3	3,644	- 6	36
4	3,650	0	0
5	3,653	3	9
6	3,636	- 14	196
7	3,651	1	1
8	3,643	- 7	49
9	3,643	- 7	49
10	3,645	- 5	25
11	3,646	- 4	16
12	3,662	12	144
13	3,840	190	36,100
14	3,902	252	63,504
15	3,652	2	4
			<hr/>
			464 - 50
			$S_1 = 414$
			<hr/>
			100,198
			$= S_2$

Hence

$$\begin{aligned}\bar{x} &= \left( \frac{414}{15} + 3,650 \right) \times 10^{-6} = 3,677.6 \times 10^{-6} \\ s &= \sqrt{\left[ \frac{1}{14} (100,198 - \frac{1}{15} \times 414^2) \right]} \times 10^{-6} \\ &= 79.6 \times 10^{-6}\end{aligned}$$

It has already been observed that this quantity  $s$  is an estimate of the standard deviation  $\sigma$ , and furthermore that the theoretical standard error of the arithmetic mean of  $n$  independent observations is  $\sigma/n^{\frac{1}{2}}$ . Hence  $s/n^{\frac{1}{2}}$  is the estimated value of the standard error of  $\bar{x}$ , or in the example just worked out

$$\text{Est. of Stand. Error of A.M.} = 79.6 \times 10^{-6}/15^{\frac{1}{2}} = 20.6 \times 10^{-6}$$

When a number of 'similar' experiments have been performed in order to measure the same quantity  $\mu$  the results may be combined in order to obtain greater accuracy. The word 'similar' here means that, not only is



the same quantity being measured in each experiment of the series, but also that the theoretical standard error of the observations is the same in each of the experiments, though of course, the estimates of  $\mu$  and  $\sigma$  in the different experiments will differ somewhat. If there are  $k$  experiments and if the number of observations in the first is  $n_1$ , their arithmetic mean  $\bar{x}_1$ , and the estimate of their standard error, obtained, as already described, from these  $n_1$  observations  $s_1$ , with similar results for the other experiments, then the estimates of the common theoretical mean and standard deviation are  $\bar{x}$  and  $s$ , where

$$\begin{aligned}\bar{x} &= \frac{1}{n}(n_1\bar{x}_1 + n_2\bar{x}_2 + \dots + n_k\bar{x}_k) = \frac{1}{n}\sum_{i=1}^k n_i\bar{x}_i, \\ &= \frac{1}{n-k}\left[\frac{\sum(x - \bar{x}_1)^2}{1} + \frac{\sum(x - \bar{x}_2)^2}{2} + \dots + \frac{\sum(x - \bar{x}_k)^2}{k}\right] \\ &= \frac{1}{n-k}[(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \dots + (n_k - 1)s_k^2] \\ &= \frac{1}{n-k}\sum_{i=1}^k (n_i - 1)s_i^2\end{aligned}$$

where  $n = n_1 + n_2 + \dots + n_k$  is the total number of observations in the series.

**Confidence or Fiducial Limits.** There are two methods in which it has been customary to summarize the results of such a series of experiments as that in Table II. They are given as

(a) Arith. Mean of Observs. ( $\pm$  Est. Stand. Error of A.M.)

(b) Arith. Mean of Observs. ( $\pm$  Est. Prob. Error of A.M.)

The only difference is the numerical factor 0.6745 in the second bracket term, but care should be taken when such summaries are being compared to note whether method (a) or (b) is being used and to make the necessary correction when the methods differ. It is much preferable to use the standard error; the 'probable error' has only tradition to recommend it.

It must be emphasized that, usually,  $\mu$  and  $\sigma$  are unknown and that, as long as this is so, no statement can be made about the probability that an observation will lie in a given range. If  $\mu$  and  $\sigma$  were known, such statements as: there is a probability of 0.998 that any observation will lie in the range  $\mu \pm 3.09\sigma$ , could be made, but it cannot be said that the probability that  $\mu$  lies in a range  $\bar{x} \pm 3.09s$  is 0.998. Unless certain assumptions about the *a priori* probability of the parameters, which are themselves to be regarded as 'random variables', are made, no probability statements about the values of the parameters have a meaning.<sup>1</sup> It is, however, possible, assuming normality, to adopt a method of fixing limits such that, for a given set of observations one can say 'almost certainly' that  $\mu$  lies within these limits. By the phrase 'almost certainly' is meant that it can be settled in advance what risk of error is to be accepted. That is, the limits are calculated in such a fashion that, in the long run, in making the statement that these limits include the 'true value' of  $\mu$  one will be wrong, say, once in

<sup>1</sup> Fisher, *Proc. Camb. Phil. Soc.*, 1930, 26, 528-35; Neyman, *J. Roy. Stat. Soc.*, 1934, 97, 589-93; Neyman, *Phil. Trans.*, 1937, 236A, 333-80.

ten times or once in fifty times. Such limits are known as 'confidence' or 'fiducial' limits, and in determining them for the theoretical mean  $\mu$  they may be expressed in the form  $\bar{x} \pm ks$ . The constant  $k$  depends on the degree of confidence needed and on the number of observations from which  $\bar{x}$  and  $s$  are calculated. When, in the long run, the limits obtained will cover the 'true value' in nine cases out of ten it is said that to the interval is attached a 'confidence coefficient' of 0.9; when the risk of error is one in fifty the 'confidence coefficient' is 0.98, and so on. The following table shows the values of  $k$  for different numbers of observations and for two levels of confidence. It should be noted that, if the standard error of  $\bar{x}$  has been estimated, the expression for the limits becomes  $\bar{x} \pm (\text{Est. Stand. Error of Arith. Mean}) \times kn^{\frac{1}{2}}$ . In the example worked out in Table II, with a 'confidence coefficient' of 0.9, the limits for  $\mu$  are  $3,713.8 \times 10^{-6}$  and  $3,641.4 \times 10^{-6}$ , while to the limits  $3,731.6 \times 10^{-6}$  and  $3,623.6 \times 10^{-6}$  may be attached a confidence coefficient of 0.98.

TABLE III

Number of observations	(a) Chance of error (b) Confidence Coefficient	
	(a) 1 in 10 (b) 0.90	(a) 1 in 50 (b) 0.98
5	0.953	1.676
10	0.580	0.892
15	0.455	0.678
20	0.387	0.568
25	0.342	0.498
30	0.310	0.449

**Errors of Functions of the Observations.** Very often the required result is calculated from several observed magnitudes. The standard error of the result may readily be obtained if the standard errors of the observed quantities are known, especially if the result is a linear function of the observations or if the errors in the observations are so small that their squares and higher powers may be neglected.

If the observations are independent and are all measured from their theoretical means, then when

$$u = a_1 z_1 + a_2 z_2 + \dots + a_n z_n = \sum_{t=1}^n a_t z_t$$

and  $z_t = x_t - \mu$ , this quantity  $u$  has a standard error of  $\sigma_u$ , with

$$\begin{aligned} \sigma_u^2 &= a_1^2 \sigma_1^2 + a_2^2 \sigma_2^2 + \dots + a_n^2 \sigma_n^2 \\ &= \sum_{t=1}^n a_t^2 \sigma_t^2 \end{aligned}$$

where, of course,  $\sigma_t$  is the standard error of  $x_t$  ( $t = 1, 2, \dots, n$ ). If the estimates of the errors  $\sigma_t$  are  $s_t$ , obtained as already described, then the

estimate of  $\sigma_u$  is  $s_u = \left[ \sum_{t=1}^n a_t^2 s_t^2 \right]^{\frac{1}{2}}$ . A particular case of this has already been mentioned, i.e. the arithmetic mean. Here  $a_1 = a_2 = \dots = a_n = \frac{1}{n}$ , and  $\sigma_1 = \sigma_2 = \dots = \sigma_n = \sigma$ , and it follows that  $\sigma_x = \sigma/n^{\frac{1}{2}}$ .

If

$$v = f(z_1, z_2, \dots, z_n)$$

and if the  $z$ 's are so small that their squares and higher powers are negligible, then, using Taylor's Theorem, it follows that approximately,

$$v = f_0 + \left( \frac{\partial f}{\partial z_1} \right)_0 z_1 + \left( \frac{\partial f}{\partial z_2} \right)_0 z_2 + \dots + \left( \frac{\partial f}{\partial z_n} \right)_0 z_n$$

where  $f_0$ ,  $\left( \frac{\partial f}{\partial z_1} \right)_0$ , &c., are the values of these quantities at their theoretical means  $z_1 = z_2 = \dots = z_n = 0$ . Assuming independence of the different observations, the formula for a linear function may be used, giving as standard error for  $v$

$$= \left[ \left( \frac{\partial f}{\partial z_1} \right)_0^2 \sigma_1^2 + \left( \frac{\partial f}{\partial z_2} \right)_0^2 \sigma_2^2 + \dots + \left( \frac{\partial f}{\partial z_n} \right)_0^2 \sigma_n^2 \right]^{\frac{1}{2}}$$

For example, the density ( $\rho$ ) of a solid may be determined by weighing it in air ( $m_1$ ) and in water ( $m_2$ ), whence

$$\rho = m_1 / (m_1 - m_2)$$

Then

$$a_1 = \frac{\partial \rho}{\partial m_1} = -m_2 / (m_1 - m_2)^2; \quad a_2 = \frac{\partial \rho}{\partial m_2} = m_1 / (m_1 - m_2)^2$$

and the values of these expressions at the mean of the observations may be used instead of their values at the theoretical means. The standard errors of  $m_1$  ( $\sigma_1$ ) and of  $m_2$  ( $\sigma_2$ ) being small and, a condition that conceivably may not be verified here, *independent*, the standard error of the density is  $\sigma_\rho$  where

$$\sigma_\rho^2 = a_1^2 \sigma_1^2 + a_2^2 \sigma_2^2$$

**Weighting and Rejection of Observations.** It sometimes happens that the conditions under which certain observations of a series are made appear to the observer to be more favourable for obtaining accurate results than others. He is inclined to attach greater importance to the values attained under the more favourable conditions and so, instead of using the arithmetic mean of the observations to estimate  $\mu$ , he takes a weighted arithmetic mean of the observations, say,  $\sum_{i=1}^n w_i x_i / \sum_{i=1}^n w_i$ , as his estimate.

The  $w$ 's attached to the more acceptable observations are larger than those attached to the observations which are considered less reliable and the standard error of this weighted mean may be calculated, as already described, if the standard error of the observations is known. If the standard error is

not known the estimate usually taken for the standard error of the weighted mean is

$$\sum_{i=1}^n w_i (x_i - \bar{x})^2 / \sum w_i (n-1) \Big|^\frac{1}{2}$$

Weighting should not be resorted to unless there are very strong reasons therefor. It is far preferable, if at all possible, to increase the number of reliable observations, and furthermore the increased care and attention, which is usually given to experiments conducted under unfavourable conditions, may more than counterbalance any disadvantage due to the conditions. No two persons will agree as to the weights to be assigned to a given series of observations, and this subjective factor makes it most undesirable to employ the method of weighting at all.

As regards the rejection of observations two different positions may arise. When the error to be expected is known *a priori* or, at least, when the order of magnitude of the standard error is known, probably from having previously performed a large number of similar experiments, a case can be made for the rejection of observations which diverge widely from the rest. When, however, little or nothing is known *a priori* of the expected standard error, and when the only estimate of the probable accuracy of the results is that obtained from the experiments in question, then the rejection of observations is definitely undesirable. This is especially so when the observations are few and, consequently, the estimate of the theoretical standard error unreliable. Even when the error is known *a priori* one can never be certain that a genuine mistake has been made in the experiment and that the divergence does not arise from an unusual, but possible, combination of accidental errors. Of course, when the experimenter knows, or suspects, that a genuine mistake or a serious variation in the conditions has occurred he is quite justified in leaving an observation out of account. The reference here is solely to a *posteriori* rejection on the grounds that one or more observations disagree with the rest. As a general working rule, when there is *a priori* knowledge of the standard error, the following may be adopted with little danger: An observation which differs from the arithmetic mean of all the observations by more than 3.5 times the standard or five times the 'probable error' may be rejected.

**Interpolation.** Very often it happens that, two quantities being connected by some relationship, the values of the dependent variable are known for certain fixed values of the independent variable and it is necessary to obtain the corresponding values at intermediate points. The simplest case, the only one dealt with here, is that which arises when the successive values of the independent variable differ by a fixed quantity. For instance, the values of  $\sin \theta$  may be tabled for values of  $\theta$  differing by minutes and  $\sin 27^\circ 34' 45''$  may be required, or instrumental readings, say, of a temperature, may be available at intervals of half a minute and the value at some intermediate time may be needed. This process of 'reading between the lines' of a table consists essentially in approximating to the relationship in question by means of a polynomial.

Suppose that the corresponding values of  $x$  and  $y$  are those given in columns 1 and 2 of Table V. In practice  $h$  is very often unity. The third

column then consists of the *first differences* of  $y$ , i.e. the differences between the successive values of  $y$  in the first column. The first differences are denoted by  $\Delta y_a$ ,  $\Delta y_{a+h}$ , &c., where  $\Delta y_a = y_{a+h} - y_a$ ,  $\Delta y_{a+h} = y_{a+2h} - y_{a+h}$ , and so on. The fourth column contains the *second differences* of  $y$ , i.e. the differences between the successive first differences. The second differences are denoted by  $\Delta^2 y_a$ ,  $\Delta^2 y_{a+h}$ , and so on, with  $\Delta^2 y_a = \Delta y_{a+h} - \Delta y_a = (y_{a+2h} - y_{a+h}) - (y_{a+h} - y_a) = y_{a+2h} - 2y_{a+h} + y_a$ , &c. The succeeding columns are formed in the same way, each from the column preceding it, and it will be found in the case of practically all tabular functions that the differences of a certain order are zero or, at least, are smaller than one unit in the last decimal place retained in the table. It is necessary, therefore, to continue the difference table only until such a point is reached, and to use only as many terms of the formulae given below as are required.

TABLE IV

$x$	$y$	First differences	Second differences	Third differences
$a - 2h$	$y_{a-2h}$			
$a - h$	$y_{a-h}$	$\Delta y_{a-2h}$		
		$\Delta y_{a-h}$	$\Delta^2 y_{a-2h}$	
$a$	$y_a$	$\Delta y_a$	$\Delta^2 y_{a-h}$	$\Delta^3 y_{a-2h}$
		$\Delta y_{a+h}$	$\Delta^2 y_a$	$\Delta^3 y_{a-h}$
$a + h$	$y_{a+h}$		$\Delta^2 y_{a+h}$	$\Delta^3 y_a$
$a + 2h$	$y_{a+2h}$	$\Delta y_{a+2h}$		$\Delta^3 y_{a+h}$
$a + 3h$	$y_{a+3h}$		$\Delta^2 y_{a+2h}$	

The value of  $x$  at which  $y$  is to be found is put in the form  $a + zh$ . The value of  $x$  which is denoted by  $a$  is suitably chosen, usually so as to make  $z$  less than unity, the difference table is constructed, and then one of the following formulae may be used to give the required value of  $y$ .

The expression

$$\frac{z(z-1)(z-2) \dots (z-p+1)}{1.2.3. \dots p}$$

being denoted by  $(z)_p$ , then

$$\begin{aligned} y_{a+zh} &= y_a + (z)_1 \Delta y_a + (z)_2 \Delta^2 y_a + (z)_3 \Delta^3 y_a \dots \\ &= y_a + (z)_1 \Delta y_a + (z)_2 \Delta^2 y_{a-h} + (z+1)_3 \Delta^3 y_{a-h} + (z+1)_4 \Delta^4 y_{a-2h} \dots \\ &= y_{a+h} + \frac{z(z^2-1^2)}{3!} \Delta^2 y_a + \frac{z(z^2-1^2)(z^2-2^2)}{5!} \Delta^4 y_{a-h} + \dots \\ &+ \xi y_a + \frac{\xi(\xi^2-1)}{3!} \Delta^2 y_{a-h} + \frac{\xi(\xi^2-1)(\xi^2-2^2)}{5!} \Delta^4 y_{a-2h} + \dots \end{aligned}$$

where

$$\xi = 1 - z$$

The last expansion is known as Everett's Formula and tables of the coefficients, for different values of  $z$ , are published in *Tracts for Computers*, No. V (Camb. Univ. Press). Very often it is quite sufficient to retain only the first two, or possible three, differences and in some cases linear interpolation, i.e. use of the first differences only, is enough.

Similar methods are available when the values of  $x$  progress by unequal steps, and may be found in any of the standard works on Interpolation.

**Method of Least Squares.** The method of least squares may be regarded merely as an empirical device for the solution of certain problems or it may be based on the normal law of error together with some other principle. This extra principle may involve the assumption that the parameters are themselves 'random variables' and the substitution of a constant for the *a priori* probability law of these parameters,<sup>1</sup> or it may involve the assumption of what is called the Method of Maximum Likelihood.<sup>2</sup> Whatever may be the basis on which the method is founded, the following examples illustrate its application to some problems which may arise.

(a) **Combination of Observations having different Standard Errors.** When dealing with the combination of the results of different experiments it was emphasized that the theoretical standard errors had to be the same in all the experiments of the series in order to justify the straightforward combination of the results. If the standard errors are known to be different the method of least squares provides a means by which the combination may be effected. Suppose that there are  $k$  experiments and that  $x_t$  is the estimate of the quantity in question obtained from the  $t$ th experiment ( $t = 1, 2, 3, \dots k$ ), while  $\sigma_t$  is the theoretical standard error of  $x_t$ . It may be that  $x_t$  is the arithmetic mean of  $n_t$  observations each of standard error  $\sigma$  so that  $\sigma_t = \sigma/n_t^{1/2}$ . The method of least squares gives as the estimate of the 'true value'  $\mu$  the value of  $x$  which minimizes the sum of squares

$$\frac{(x_1 - x)^2}{\sigma_1^2} + \frac{(x_2 - x)^2}{\sigma_2^2} + \frac{(x_3 - x)^2}{\sigma_3^2} + \dots + \frac{(x_k - x)^2}{\sigma_k^2} = \sum_{t=1}^k \frac{(x_t - x)^2}{\sigma_t^2}$$

that is

$$x = \frac{\sum_{t=1}^k x_t \sigma_t^{-2}}{\sum_{t=1}^k \sigma_t^{-2}}$$

Hence the estimate taken is a weighted arithmetic mean of the quantities  $x_t$ , the weights being proportional to the reciprocals of their theoretical variances. If, as above,  $\sigma_t = \sigma/n_t^{1/2}$  then the above formula becomes

$$x = \frac{\sum_{t=1}^k x_t n_t}{\sum_{t=1}^k n_t}$$

(b) **Curve Fitting.** When a variable  $y$  depends on another variable  $x$  a polynomial may be fitted to the corresponding pairs of values, in order to obtain some idea of their relationship. When the number of pairs of values of  $x$  and  $y$  available is the same as the number of constants to be determined in the polynomial, i.e. one more than the degree of the relation, it is possible

<sup>1</sup> Neyman, *Phil. Trans.*, 1937, 234A, 344.

<sup>2</sup> Fisher, *Phil. Trans.*, 1922, 222A, 309-68.

to get a curve which will pass exactly through all the points corresponding to the pairs of values of  $x$  and  $y$ . For instance, a straight line can be got to pass through two points, a curve of the second degree, such as  $y = \alpha + \beta x + \gamma x^2$ , through three points, and so on. All that is necessary is to substitute in the above relation the corresponding values of  $x$  and  $y$  and to solve the resulting equations for  $\alpha$ ,  $\beta$ ,  $\gamma$ . When the values of  $x$  available differ by a constant amount the easiest way to get the relation is to use the method of differencing and interpolation already explained. Very often, however, the need may arise to fit a curve to a long series of observations, and, while keeping the degree of the curve low, to utilize all the observations in determining the constants. Using the method of least squares, the procedure is to choose those values of the constants which minimize  $\Sigma[y - f(x)]^2$ ,  $y = f(x)$  being the curve to be fitted and the summation extending to all the pairs of observations.

For instance, to fit the straight line  $y = \alpha + \beta x$  to a series of pairs of values of  $x$  and  $y$  the values of  $\alpha$  and  $\beta$  taken are those values of  $a$  and  $b$  which minimize  $S = \Sigma(y - a - bx)^2$  and the equations for  $a$  and  $b$  are

$$\frac{\partial S}{\partial a} = 0, \text{ or } \Sigma(y - a - bx) = 0 = n\bar{y} - a.n - b.n\bar{x}$$

$$\frac{\partial S}{\partial b} = 0, \text{ or } \Sigma x(y - a - bx) = 0 = \Sigma xy - a.n\bar{x} - b.\Sigma x^2$$

whence

$$a = \frac{\bar{y}\Sigma x^2 - \bar{x}\Sigma xy}{\Sigma x^2 - n\bar{x}^2} = \bar{y} - b.\bar{x}$$

$$b = \frac{\Sigma xy - n\bar{x}\bar{y}}{\Sigma x^2 - n\bar{x}^2} = \frac{\Sigma y(x - \bar{x})}{\Sigma (x - \bar{x})^2}$$

the second expressions being readily deducible from the others. These values for  $a$  and  $b$  give the 'best', or 'expected' values of  $y$  for each value of  $x$ . They do not give the 'best' expression for the relation between  $y$  and  $x$ , nor can it be said, as it often is, that  $x = (y - a)/b$  is the 'expected' value of  $x$  for a given  $y$ ; to obtain this the expression  $\Sigma(x - p - qy)^2$  must be minimized as before and the values thus got for  $p$  and  $q$  used.

To fit, in similar fashion, the equation  $y = \alpha + \beta x + \gamma x^2$  to the observations the estimates of  $\alpha$ ,  $\beta$ , and  $\gamma$  are  $a$ ,  $b$ ,  $c$ , where these quantities minimize  $\Sigma(y - a - bx - cx^2)^2$ . The equations for  $a$ ,  $b$ , and  $c$  are

$$\begin{aligned} n\bar{y} - a.n - b.n\bar{x} - c.\Sigma x^2 &= 0 \\ \Sigma xy - a.n\bar{x} - b.\Sigma x^2 - c.\Sigma x^3 &= 0 \\ \Sigma x^2 y - a.\Sigma x^2 - b.\Sigma x^3 - c.\Sigma x^4 &= 0 \end{aligned}$$

Similar equations may be found for fitting curves of higher degrees, but the labour needed for their solution increases rapidly with the number of constants. A device known as fitting by Orthogonal Polynomials is employed in the fitting of higher degree curves.<sup>1</sup>

When a variable, say  $w$ , depends on a number of others, say  $x$ ,  $y$ ,  $z$ , and a series of observations give corresponding values of these quantities, then

<sup>1</sup> Fisher, *Phil. Trans.*, 1924, 213B, 89-142; Fisher, *Statistical Methods for Research Workers* (Oliver & Boyd, 1936), pp. 148 et seq.; Allen, *Proc. Roy. Soc. Edin.*, 1929, 5, 310-20.

if the ' expected ' value of  $w$  can be expressed in the form  $\alpha + \beta x + \gamma y + \delta z$ , estimates of the quantities  $\alpha, \beta, \gamma, \delta$ , can, similarly, be made by the method of least squares. The estimates taken are the values of  $a, b, c, d$ , which minimize

$$\Sigma(w - a - bx - cy - dz)^2$$

the summation as usual extending to all the  $n$  corresponding sets of observations. The equations for  $a, b, c, d$ , are

$$\begin{aligned}\bar{w} - a - b.\bar{x} - c.\bar{y} - d.\bar{z} &= 0 \\ \Sigma wx - a.n\bar{x} - b.\Sigma x^2 - c.\Sigma xy - d.\Sigma xz &= 0 \\ \Sigma wy - a.n\bar{y} - b.\Sigma xy - c.\Sigma y^2 - d.\Sigma yz &= 0 \\ \Sigma wz - a.n\bar{z} - b.\Sigma xz - c.\Sigma yz - d.\Sigma z^2 &= 0\end{aligned}$$

These equations may be solved by the methods explained in the next paragraph.

(c) **Indirect Observations involving more than one unknown.**

The next case to be considered is when the quantity measured is not itself the unknown we require, but is expressible as a given function of a number of unknown quantities which may or may not be linear.

Let the observed quantities be  $M_1, M_2, \dots M_n$ , and let the unknown errors be  $v_1, v_2, \dots v_n$ . Then, if the unknowns be  $X, Y$ , and  $Z$ ,

$$\begin{aligned}f_1(X.Y.Z \dots) &= M_1 + v_1 \quad . \quad . \quad . \quad . \quad (1) \\ f_2(X.Y.Z \dots) &= M_2 + v_2\end{aligned}$$

&c.

The number ( $n$ ) of observations is greater than the number ( $m$ ) of unknowns. Approximate values of the unknowns can be found by substitution in a sufficient number of the equations (1). Let these approximate values be  $X_0, Y_0, Z_0$ , and let  $X = X_0 + x, Y = Y_0 + y$ , &c., where  $x, y$ , &c., are so small that  $x^2, y^2$ , &c., are negligible. Equation (1) may then be written

$$f_1(X_0.Y_0.Z_0) + x \cdot \frac{df_1}{dX_0} + y \cdot \frac{df_1}{dY_0} + z \cdot \frac{df_1}{dZ_0} = M_1 + v_1$$

$$\text{Let} \quad \frac{df_1}{dX_0} = a_1, \quad \frac{df_1}{dY_0} = b_1, \quad \&c.$$

$$\text{and} \quad \frac{df_2}{dX_0} = a_2, \quad \frac{df_2}{dY_0} = b_2 \quad \&c.$$

$$\begin{aligned}\text{and} \quad f_1(X_0.Y_0.Z_0 \dots) - M_1 &= l_1 \\ f_2(X_0.Y_0.Z_0 \dots) - M_2 &= l_2\end{aligned}$$

Then equation (1) may be written

$$\begin{aligned}a_1x + b_1y + c_1z \dots - l_1 &= v_1 \quad . \quad . \quad . \quad . \quad (2) \\ a_2x + b_2y + c_2z \dots - l_2 &= v_2\end{aligned}$$

&c. The equations are now linear and the values of  $a, b, c, l$ , &c., are known.

If the values of  $x, y$ , and  $z$ , obtained by solving the equations, are not small, they may be used to get closer approximations to the values of  $X, Y$ , and  $Z$ , and the process be repeated. Even when the original equations are linear, calculations are often appreciably shortened by using approximate values for the constants. When the number of unknowns is less than the



number of observations (and therefore equations), by taking those values of the unknowns which minimize the sum of squares

$$\Sigma(ax + by + cz + \dots - l)^2$$

the number of equations may be reduced to the number of unknowns and then solved. The conditions for a minimum, with respect to  $x, y, z, \dots$  are

$$\begin{aligned} a_1(a_1x + b_1y + c_1z \dots - l_1) + a_2(a_2x + b_2y \dots - l_2) + \&c. &= 0 \\ b_1(a_1x + b_1y + c_1z \dots - l_1) + b_2(a_2x + b_2y \dots - l_2) + \&c. &= 0 \end{aligned}$$

&c.

and collecting coefficients

$$\begin{aligned} [aa]x + [ab]y + [ac]z + \dots - [al] &= 0 \\ [ab]x + [bb]y + [bc]z + \dots - [bl] &= 0 \\ [ac]x + [bc]y + [cc]z + \dots - [cl] &= 0 \end{aligned}$$

&c.

where

$$\begin{aligned} [aa] &= a_1^2 + a_2^2 + \dots \\ [ab] &= a_1b_1 + a_2b_2 + \dots \end{aligned}$$

These are the 'normal equations', and we have now reduced the number of equations to equal the number of unknowns. The coefficients of the normal equations are symmetrical about the principal diagonal, so that we can abbreviate them to

$$\begin{aligned} [aa]x + [ab]y + [ac]z + \dots - [al] &= 0 \\ + [bb]y + [bc]z + \dots - [bl] &= 0 \\ + [cc]z + \dots - [cl] &= 0 \end{aligned}$$

&c.

In forming the normal equations a check is necessary and the following will be found convenient.

$$\text{Let} \quad a_r + b_r + c_r \dots + l_r = s_r$$

multiply each  $s$  equation by the corresponding  $a$  and add, then

$$\begin{aligned} [aa] + [ab] + \dots [al] &= [as] \\ [ba] + [bb] + \dots [bl] &= [bs] \end{aligned}$$

In a piece of work involving a large number of equations it is advisable to work according to fixed system, so that the whole work including the application of checks becomes as mechanical as possible.

When the number of unknowns is not greater than two or when the  $c$  coefficients are integral, the solution can be carried out by ordinary algebraic methods. But in all cases it is better to use the method of Gauss or Doolittle's variation thereof, which reduces the number of entries to be made.

Using the normal equations already obtained from the first, we get

$$x = -\frac{[ab]}{[aa]}y - \frac{[ac]}{[aa]}z + \frac{[al]}{[aa]} \quad (3)$$

and substituting this in the second and third

$$\begin{aligned} [bb]y + [bc]z - [bl] &= 0 \\ [bc]y + [cc]z - [cl] &= 0 \end{aligned} \quad (4)$$

where 
$$[bb1] = [bb] - \frac{[ab][ab]}{[aa]}$$

$$[bc1] = [bc] - \frac{[ab][ac]}{[aa]}$$

From the first equation in (4)

$$y = -\frac{[bc1]z}{[bb1]} + \frac{[bl1]}{[bb1]} \quad (5)$$

and putting this in the equation (4ii)

$$[cc2]z - [cl2] = 0 \quad (6)$$

where

$$[cc2] = [cc1] - \frac{[bc1][bc1]}{[bb1]}$$

$$[cl2] = [cl1] - \frac{[bc1][bl2]}{[bb1]}$$

Equation (6) gives  $z$ , and this value substituted in (5) gives  $y$ , and putting  $y$  and  $z$  in equation (3) gives  $x$ .

#### Checks in Computation.

1. The leading coefficients  $[aa]$ ,  $[bb1]$ ,  $[cc2]$  must all be positive.
2. In checking the formation of the normal equation we used

$$[as], [bs], [cs] \dots [ls]$$

Operating in the same way upon these quantities as we did upon  $[al]$ ,  $[bl]$ , &c., we can obtain the new quantities  $[bs1]$ ,  $[cs1]$ ,  $[cs2]$ , &c., and for the three unknowns

$$\begin{aligned} [bb1] + [bc1] + [bl1] &= [bs1] \\ [bc1] + [cc1] + [cl1] &= [cs1] \\ [cc2] + [cl2] &= [cs2] \end{aligned}$$

3. When the three unknowns have been evaluated and substituted in the observational equations we can get the residuals,  $v_1$ ,  $v_2$ , &c., then

$$[av] = [bv] = [cv] = \dots = 0$$

These checks should be sufficient to detect any error in the computation. Doolittle's form of solution saves considerable labour in computation and is illustrated for the equations

$$\begin{aligned} [aa]x + [ab]y + [ac]z &= [al] \\ [bb]y + [bc]z &= [bl] \\ [cc]z &= [cl] \end{aligned}$$

and is shown in Tables V and VI.

The coefficients of the first normal equation are written in line 1, Table V. The reciprocal of  $[aa]$  with its sign changed is written in the first column, and used to multiply all the other quantities in line 1, thus giving line 2. Line 2 then gives  $x$  as an explicit function of  $y$  and  $z$ .

The coefficients of the second normal equation are written in line 1, Table VI. Line 2, Table V, is multiplied by  $[ab]$ , giving line 2, Table VI. The sum of lines 1 and 2, Table VI, gives line 3, Table V. The reciprocal of  $[bb1]$  with sign changed is written in column 1, Table V, and used to

TABLE V

	$x$	$y$	$z$	
$-\frac{1}{[aa]}$	$[aa]$ $x =$	$[ab]$ $-\frac{[ab]}{[aa]}$	$[ac]$ $-\frac{[ac]}{[aa]}$	$-[al]$ $\frac{[al]}{[aa]}$
$-\frac{1}{[bb1]}$		$[bb1]$ $y =$	$[bc1]$ $-\frac{[bc1]}{[bb1]}$	$-[bl1]$ $+\frac{[bl1]}{[bb1]}$
$-\frac{1}{[cc2]}$			$[cc2]$ $z =$	$-[cl2]$ $\frac{[cl2]}{[cc2]}$

multiply line 3, giving line 4. This line gives  $y$  as an explicit function of  $z$ . The coefficients of the third normal equation are written in line 3, Table VI.

The second line of the fourth and fifth columns of Table V is multiplied by  $[ac]$  to give line 4, Table VI, and the fourth line of the same two columns in Table V when multiplied by  $[bc1]$  gives line 5 of Table VI. The sum of lines 3, 4, and 5 of Table VI gives line 5 of Table V, and from this line 6 is obtained, giving the value of  $z$ .

$z$  and line 4 of Table V then give  $y$ , and  $y$  and  $z$  with line 2 of Table V give  $x$ .

TABLE VI

$y$	$z$	
$[bb]$ $-\frac{[ab][ab]}{[aa]}$	$[bc]$ $-\frac{[ab][ac]}{[aa]}$	$-[bl]$ $\frac{[ab][al]}{[aa]}$
	$[cc]$ $-\frac{[ac][ac]}{[aa]}$	$-[cl]$ $\frac{[ac][al]}{[aa]}$
	$-\frac{[bc1][bc1]}{[bb1]}$	$\frac{[bc1][bl1]}{[bb1]}$

## SECTION 2: NOMOGRAPHY

During recent years the solution of equations and evaluation of results have been largely accomplished by graphical methods. The accuracy of graphical construction is on a level with that of the slide rule. Where numbers of calculations from the same formula are necessary, its rapidity is much greater than that obtained by other methods of calculation. Further, such methods afford a general examination of the variation of a result with change in the individual factors.

Among graphical methods at present in use a foremost place is occupied by *nomography*, the science of the graphical representation of functions. In the following pages the theoretical development of the subject is not expounded in any detail; the object rather has been to demonstrate the use of the nomogram in certain types of formulae useful to the physical chemist.

If we have a formula connecting two variable quantities  $a$  and  $b$ , we can draw a curve showing the relationship between  $a$  and  $b$ , by giving certain values to  $a$ , from the formula calculating the corresponding values of  $b$ , and plotting the values  $a$  and  $b$  using rectangular axes and suitable scales for  $a$  and  $b$ . From this curve, then, any value of  $b$  corresponding to a given value of  $a$  can be obtained.

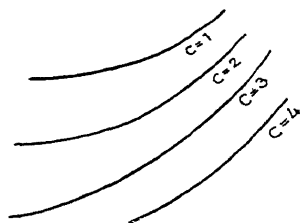


FIG. 3 (IV)

Where the formula includes three variable quantities  $a$ ,  $b$ , and  $c$ , we can apply the same method and construct a family of curves as in Fig. 3 (IV), representing the formula, by giving  $c$  certain values and drawing the corresponding  $ab$  curve as before.

To use the diagram to obtain the value of  $c$  corresponding to given values of  $a$  and  $b$ , we obtain the point of intersection of the lines  $x = a$ ,  $y = b$ , and see in which curve the point falls. If, as is likely, it does not fall on any of the curves already drawn, interpolation between the curves must be performed. Obviously this is a difficult process for obtaining accurate values. To simplify this interpolation and make more accurate reading possible the system of curves ( $c$ ) is represented by a single curve graduated according to the values of  $c$  for corresponding values of  $a$  and  $b$ . This transformation is effected as follows. Instead of the evenly divided scales proportional to  $a$  and  $b$  as  $x$  and  $y$  respectively, we substitute scales divided in proportion to function ( $a$ ) and function ( $b$ ) as they occur in the original formula. The system of curves ( $c$ ) now become systems of straight lines. For instance, if the function of  $a$  occurring in the original formula is  $\log a$ , the graduation marks 1, 2, 3, 4 along the  $x$  axis are placed at the distances  $\log 1$ ,  $\log 2$ ,  $\log 3$ ,

$\log 4$ , from the origin. Similarly the graduations on the  $y$  axis are placed at the values of function ( $b$ ). The curves then practically become straight lines, such as shown in Fig. 4 (IV). These do not correspond in the particular example given with the curves of Fig. 3 (IV).

To represent  $c$  as a single line the device of using parallel axes for plotting  $a$  and  $b$  rather than rectangular ones is adopted. For any fixed value of  $c$ , with rectangular co-ordinates, the relation of function ( $a$ ) to function ( $b$ ) can be represented by a straight line as has been seen. With parallel axes this straight line changes to a point, as for this fixed value of  $c$  all the straight

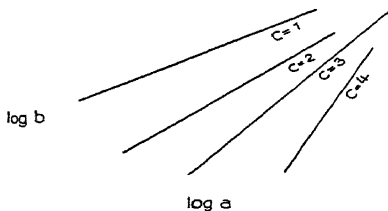


FIG. 4 (IV)

FIG. 5 (IV)

lines connecting corresponding values on the  $a$  and  $b$  axes will meet in a point. Conversely any straight line drawn through this point will cut the  $a$  and  $b$  axes in values which will satisfy the equation for that particular value of  $c$ . Instead therefore of a system of straight lines a system of points is secured which can be joined into a curve. The curve is graduated according to the values of  $c$  given to each point. This is the nomogram proper (Fig. 5 (IV)).

It is also known as the 'alignment diagram', as the value of  $c$ , corresponding to values of  $a$  and  $b$ , is found by aligning these values and determining where the curve of  $c$  is intersected. The curve  $c$  will be a straight line if the corresponding system of straight lines (with rectangular axes) meet in a point.

Alignment diagrams may be divided into types or groups.

Type I. If the formula to be represented can be put in the form

$$f_1(a) + f_2(b) = f_3(c), \text{ [} f \text{ represents function]}$$

the three systems of points  $a$ ,  $b$ , and  $c$  can be arranged along three parallel lines.

Let  $Ax$ ,  $By$ , and  $Cz$  be three parallel axes with  $ABC$  any transversal or base line (Fig. 6 (IV)). Draw any transversal cutting the axes in  $a$ ,  $b$ ,  $c$  respectively so that  $Aa = x$ ,  $Bb = y$ ,  $Cc = z$ . If  $AC : CB = k_1 : k_2$  and if through  $b$  and  $c$  we draw lines parallel to  $ABC$  then the triangles  $acE$  and  $bcD$  are similar, and  $Ea : De = Ec : Db = AC : CB$ .

or

$$x - z : z - y = k_1 : k_2$$

$$\therefore k_2x + k_1y = (k_1 + k_2)z$$

or

$$\frac{x}{k_1} + \frac{y}{k_2} = \frac{z}{\frac{k_1k_2}{k_1 + k_2}}$$

If  $Ax$ ,  $By$ ,  $Cz$  carry the scales

$$x = k_1 f_1(a), \quad y = k_2 f_2(b)$$

$$z = \frac{k_1 k_2}{k_1 + k_2} f_3(c)$$

respectively, the last equation becomes  $f_1(a) + f_2(b) = f_3(c)$ , and any index line will cut the axes in three points whose corresponding values  $a$ ,  $b$ ,  $c$  satisfy this equation.

Hence to construct a nomogram for equations of the form

$$f_1(a) + f_2(b) = f_3(c)$$

draw two parallel axes a distance apart, and on these construct the scales  $x = k_1 f_1(a)$  and  $y = k_2 f_2(b)$ , where  $k_1$  and  $k_2$  are convenient moduli. A third axis is then drawn parallel to the others at such a distance from them that

$$\begin{aligned} (\text{distance from } x \text{ axis to } z \text{ axis}) : (\text{distance from } z \text{ axis to } y \text{ axis}) \\ = k_1 : k_2 \end{aligned}$$

On this axis construct a scale

$$z = \frac{k_1 k_2}{k_1 + k_2} f_3(c)$$

A fixed point on this axis must be selected as a starting-point so that the value on the  $z$  axis corresponds to the aligned values on the  $x$  and  $y$  axis as computed from the original equation. If the points  $A$ ,  $B$ ,  $C$ , occur on the scale the point  $C(z = 0)$  is the most convenient as origin.

In reading the scale the index line need not be drawn; any straight edge can be used for indicating corresponding values. A line cut on transparent celluloid is usual.

The equation  $f_1(a)f_2(b) = f_3(c)$  can be charted this way, as it can be put in the form  $\log f_1(a) + \log f_2(b) = \log f_3(c)$ , also the equation  $f_1(a) - f_2(b) = f_3(c)$  may be charted by plotting the  $x$  and  $y$  scales in opposite directions.

A simple example of this type of diagram is a multiplication and division chart. The equation is  $a \cdot b = c$ .

If we write this as  $\log a + \log b = \log c$ , the equation is of the given form. Let  $a$  and  $b$  range from 1 to 10; then  $c$  ranges from 1 to 100. Construct the parallel scales

$$\begin{aligned} x &= k_1 \log a = 10 \log a \\ y &= k_2 \log b = 10 \log b \end{aligned}$$

Since  $k_1 : k_2 = 1 : 1$ , the  $z$  axis is midway between the  $x$  and  $y$  axes. The line joining  $a = 1$  and  $b = 1$  must cut the two axes in  $c = 1$ . Using this as a starting-point, we construct the scale

$$z = \frac{k_1 k_2}{k_1 + k_2} \log c = 5 \log c$$

and the diagram is complete.

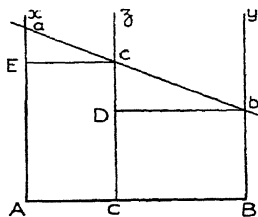


FIG. 6 (IV)

A commonly met equation  $PV^\gamma = C$ , may be charted similarly ( $\gamma = 1.41$ , its value for certain gases).

If we chose  $k_1 = 10$  and  $k_2 = \frac{10}{1.41} = 7.092$

$$k_3 = \frac{k_1 k_2}{k_1 + k_2} = 4.15$$

The equations of the scales are therefore  $x = 10 \log P$ ,  $y = 7.092 \log V$ ,  $z = 4.15 \log C$ , and  $k_1 : k_2 = 1.41 : 1$ .

In a great number of alignment diagrams, as in the above example,

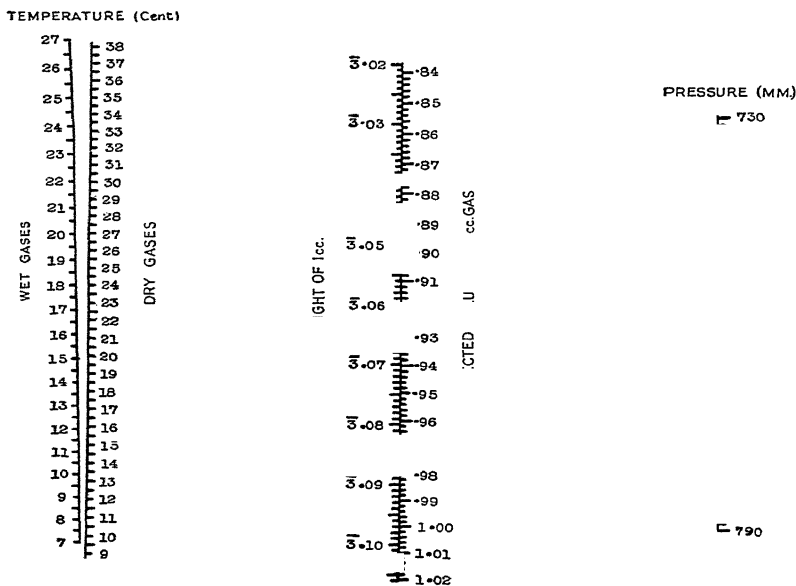


FIG. 7 (IV)

logarithmic scales are needed; they can be projected directly from a fixed scale, thereby greatly saving time and trouble.

Farmer's gas calculator<sup>1</sup> is a nomographic chart for converting gas volumes to standard conditions. A reduced representation of the chart is shown (Fig. 7 (IV)). Where frequent gas calculations are carried out, its utility is obvious.

By the use of this graphic method the corrected volume of 1 ml. of gas, either wet or dry, can be found with an accuracy of about 2 parts in 10,000 in one single operation. In this manner errors are avoided and a great saving of time and work on gases is secured.

A cursor is laid across the diagram joining the points indicating the tem-

<sup>1</sup> Published by Baird & Tatlock, London,

perature and pressure at which the gas was measured, and the corrected volume is read off directly. Conversely, the temperature or pressure can be found if the volume is known. The logarithm of the corrected weight of nitrogen can be read off at the same time, thus reducing the calculation of 'nitrogen percentages' to a very simple operation.

Type II. Where four or more variables occur in the equation an extension of the method is necessary. Let the equation have the form :

$$f_1(a) + f_2(b) + f_3(c) = f_4(d)$$

Let

$$f_1(a) + f_2(b) = q \quad \dots \quad (1)$$

Equation (1) is of type I and can be charted by means of three parallel scales  $f_1(a)$ ,  $f_2(b)$  and  $q$ . The  $q$  scale need not be graduated (Fig. 8 (IV)).

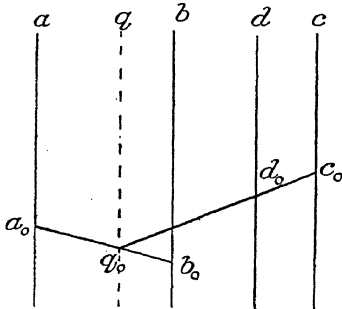


FIG. 8 (IV)

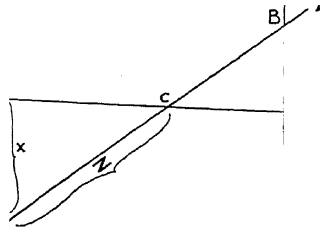


FIG. 9 (IV)

We then have  $q + f_3(c) = f_4(d)$ , which can also be charted with three parallel scales. In the process the  $q$  scale is made identical with the one already drawn. The graduations of the  $a$ ,  $b$ , and  $c$  scales may begin anywhere on their axes, but the starting-point of the ( $d$ ) scale must be found from a set of values  $a_0$ ,  $b_0$ ,  $c_0$ ,  $d_0$ , satisfying the original equation. Join  $a_0$  and  $b_0$  and hence determine  $q_0$ . Join  $q_0$  and  $c_0$ , the intersection with the  $d$  axis must be  $d_0$ .

The same procedure is adopted in reading the completed scale.

A great number of equations, therefore, can be represented with parallel axes either directly or by transformation with logarithms. In some cases it is preferable to avoid the latter contingency and plot three natural scales with the third axis oblique to the others.

Type III. Equations of the form  $f_1(a) = f_2(b).f_3(c)$  or  $f_1(a) = f_3(b)f_3(c)$ .

The first form has already been treated by the use of logarithmic scales.

In Fig. 9 (IV) let AX and BY be two parallel scales and AZ any axis oblique to these, and cutting them in A and B respectively. Draw any index line cutting the axis in  $a$ ,  $b$ ,  $c$ , so that  $Aa = x$ ,  $Bb = y$ ,  $Ac = z$ . Let  $AB = k$ . Then in the similar triangles  $Aac$ ,  $Bbc$

$$Aa : Bb = Ac : cB$$

or

$$x : y = z : k - z$$

or

$$x = \frac{z}{k} \cdot y$$



If AX and BY carry the scales  $x = k_1 f_1(a)$ , and  $y = k_2 f_2(b)$ , the last equation becomes  $(a) = \frac{k_2 z}{k_1(k-z)} f_2(b)$ , and, if AZ carries a scale for C such that

$$\frac{k_2 z}{k_1(k-z)} = f_3(c) \text{ or } z = k \frac{k_1 f_3(c)}{k_1 f_3(c) + k_2}$$

the equation becomes  $f_1(a) = f_2(b) \cdot f_3(c)$ , and any index line will cut the axis in three corresponding points.

To chart the equation:

Draw three axes AX, BY, and AB, where AX and BY are parallel and oppositely directed and AB is any convenient length  $k$ . With A and B as origins construct the scales

$$x = k_1 f_1(a), \quad y = k_2 f_2(b), \quad z = k \frac{k_1 f_3(c)}{k_1 f_3(c) + k_2}$$

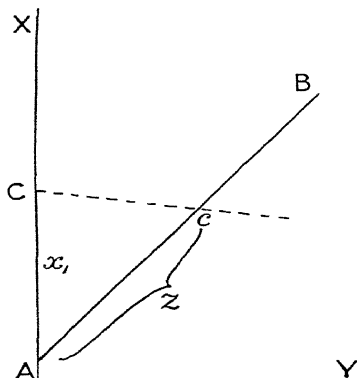


FIG. 10 (IV)

For the construction of the  $c$  scale, it is necessary to compute the value of  $z$  for every value of  $c$  which is to appear on the chart; to avoid this: on BY choose a fixed point F at any convenient distance,  $l$ , from B (Fig. 10 (IV)), and on AX construct the scale

$$AC = x_1 = \frac{k_1}{k_2} f_3(c)$$

From F as centre, project the points C on the axis AB. Let FC cut AB in  $c$  and let  $Ac = z$ . Then in the similar triangles ACc and BFc

$$\begin{aligned} z : k - z &= x_1 : l \text{ or } z = \frac{kx_1}{l + x_1} \\ &= k \frac{k_1 f_3(c)}{k_1 f_3(c) + lk_2} \end{aligned}$$

Hence we construct the scale  $x = \frac{k_1}{k_2} f_3(c)$  on AX, and then project this scale from the fixed point F on BY to the axis AB, marking corresponding points with the same value of  $c$ .

It may also be shown that an equation of the form  $\frac{f_1(a)}{f_2(b)} = \frac{f_3(c)}{f_4(d)}$  may be represented by drawing the parallel axes AX and BY and the parallel axes AB and BT through the ends of AB (diagram not given). AB may coincide or make any angle with AX and similarly with BY and BT. On these axes construct the scales  $x = k_1 f_1(a)$ ,  $y = k_2 f_2(b)$ ,  $z = k_3 f_3(x)$ , and  $i = k_4 f_4(d)$ , where  $k_1 : k_2 = k_3 : k_4$ .

To read the chart use two index lines, one joining  $a$  and  $b$  and the other  $c$  and  $d$ . They will intersect on a point on AB.

A universal or flexible nomograph has been devised by McMullen <sup>1</sup> in which the use of a number of separate nomographs are combined. A copy of this chart is given in the reference indicated. In many practical operations it is necessary to calculate certain variables or coefficients.<sup>2</sup> This universal nomograph may be used to simplify these calculations. An outcome of this work is the production of a combined nomograph and slide rule capable of performing all the operations possible on the above chart, without the multiplicity of unscaled lines corresponding to the various components (see next section).

<sup>1</sup> *Ind. and Eng. Chem.*, 1938, 30, 71.

<sup>2</sup> *Ibid.*

### SECTION 3: SLIDE RULE

Where many calculations are required to an accuracy of 1 part in 1,000 the ordinary arithmetic procedure is often tedious ; for example, where the results of a long series of observations are being calculated the labour involved is considerable ; a rapid method of calculation is essential, and that at present in general use is the employment of the calculating instrument known as the slide rule. This instrument, based on strict mathematical principles, gives direct results for all arithmetical processes, without mental effort on the part

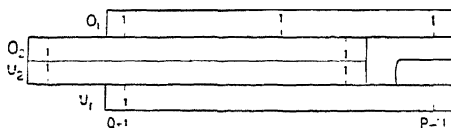


FIG. 11 (IV)

of the manipulator. A 20-inch rule gives results accurate to 1 in 1,000, while the ordinary pocket 10-inch rule gives results correct to 1 in 500.

The slide rule consists of three essential parts : the *rule* or fixed portion ; the *slider* which runs along a groove in the rule ; and the cursor, a simple transparent arrangement for sliding on the rule lengthwise and worked with a zero line on the transparent portion. This aids in the setting of the slider and in reading off the numbers, as well as fixing the intermediate steps of a calculation. The *rule* has an upper scale  $O_1$  and a lower scale  $U_1$  (Fig. 11 (IV) ). On the front of the slider there is an upper scale  $O_2$  and a lower scale

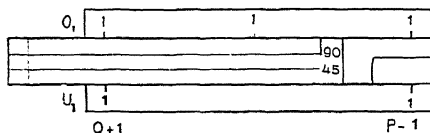


FIG. 12 (IV)

$U_2$  ; on the back of the slider are the scales S, L, and T (Fig. 12 (IV) ). Of these scales  $O_1$  and  $O_2$  correspond, as also  $U_1$  and  $U_2$ . All the scales have been obtained by taking the whole length of the scale as a logarithmic unit and dividing this into lengths which are proportional to the logarithms of the numbers placed alongside the scale marks. The numerical values of the logarithms of the numbers from 1 to 100 are marked off on the two scales as lengths, the divisions being marked with numbers which correspond not to the lengths but to the logarithms of the lengths. For the scales  $U_1$ ,  $U_2$ , T and L the length of the logarithmic unit is 25 cm. For the scales  $O_1$ ,  $O_2$  and

Since the length of the logarithmic unit is only 12.5 cm. In the case of these scales therefore there are two logarithmic units in the length of 25 cm. By reason of the method of graduation of the scales, calculations with the slide rule are carried out in accordance with the same rules and principles as calculations with logarithms. As

$$\log ab = \log a + \log b$$

$$\log \frac{a}{b} = \log a - \log b$$

$$\log \sqrt[n]{a} = \frac{1}{n} \log a$$

The arithmetic processes of multiplication, division, and root extraction, in the case of the slide rule becomes processes of addition, subtraction, and subdivision of logarithmic lengths.

**Multiplication.** To obtain a product  $mn$ , the cursor is brought to  $m$  on the top scale and the 1 (or 10) on the slide is brought to coincidence with  $m$ , the cursor is then moved to  $n$  on the slide, and the reading of the top rule coinciding with  $n$  gives the product  $mn$ , i.e. the two lengths corresponding to the logs of  $m$  and  $n$  are added and the sum of course gives the length corresponding to the log of  $mn$ . Or, in more detail, to carry out the process of multiplication place the initial mark 1 on the slider  $U_2$  opposite the number  $a$  on the scale  $U_1$  and look for the number  $b$  on the scale  $U_2$ . The mark on  $U_1$  which is in coincidence with this mark  $b$  represents the sum of the lengths  $a$  and  $b$  and the corresponding number gives the magnitude of the product  $ab$  (Fig. 13 (IV)).

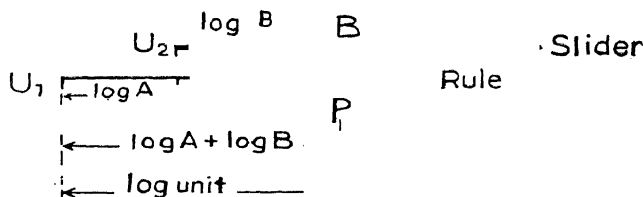


FIG. 13 (IV)

**Division.** As shown above, the process of division with the slide rule becomes one of subtraction. To divide  $p$  by  $q$  the cursor is placed over  $p$  on the top scale;  $q$  on the slide is then brought to coincidence with  $p$ . The cursor is then moved to 1 on the slide and the figure on the top scale coincident with it is the required result—the logarithms of the numbers have been subtracted. If when  $p$  coincides with  $q$ , the 1 on the slide is off the upper scale, we can equally well take the reading corresponding to 10 or 100 on the scale. Or, in detail, place the number  $b$  on the slider scale  $U_2$  in coincidence with the number  $a$  on the rule scale  $U_1$  and subtract from the length corresponding with the logarithm of  $a$  the length corresponding with the logarithm of  $b$ . The number on  $U_1$  opposite to the initial mark on the scale  $U_2$  represents the quotient  $\frac{a}{b}$ . When  $a$  is greater than  $b$ , when the reading therefore is opposite the initial mark, then the result is read off on the left of the setting. When  $b$

is greater than  $a$ , when the reading is therefore opposite the end mark, the result is read off at the right of the setting. The position of the decimal point is found by rough calculation.

**Squares and Square Roots.** As stated in the description of the slide rule, the dimensions of the scales  $U_1$  and  $U_2$  are twice those of the scales  $O_1$  and  $O_2$ . Each logarithmic distance on the scales  $U_1$  and  $U_2$  corresponds therefore with twice this logarithmic distance on the scales  $O_1$  and  $O_2$ . As the scales are logarithmic it follows that the numbers on  $O_1$  lying perpendicularly above the numbers on  $U_1$  correspond with the squares of these numbers, and conversely those on  $U_1$  correspond with the square roots of those on  $O_1$ . This also holds for the scales  $U_2$  and  $O_2$ . Hence, by the aid of the marked line on the cursor, the slide rule may be used directly for evaluating squares and square roots.

**Cubes and Cube Roots.** To find the value  $a^3$  the process becomes that of multiplying  $a$  by  $a^2$ . Place the initial or end mark of the slider in coincidence with the number  $a$  on the scale  $U_1$  or  $O_1$ . Directly above  $a$  we have the square of  $a$ . The process is now multiplication. Keeping the position of the slider unchanged, on the scale  $O_1$  add to the length  $a^2$  the length  $a$  on the one-place scale  $O_2$  and opposite to this number read off the value of  $a^3$  on the scale  $O_1$ .

To determine the cube root place the cursor line over the cube number on the scale  $O_1$ , and move the slider until the number on the scale of  $O_2$  is the same as that on the scale  $U_1$ , opposite the initial or end mark of  $U_2$ . This then is the cube root. The process is simply the reverse of the preceding.

**Logarithms.** The taking of logarithms, raising to powers or extracting roots, which are fractional or greater than 3, is accomplished with the help of the scale  $L$  on the back of the slider. To find the logarithm of a number, place the initial mark of  $U_2$  opposite the number  $a$  on  $U_1$ , turn the slide rule around and read off the mantissa of the logarithm of  $a$  on the 'L' scale, opposite the mark on the notch in the reverse side of the rule. The operation can, of course, be reversed.

**Higher Powers and Roots.** The power of a number is determined by multiplying the logarithm of the number by the power. This is accomplished by the 'L' scale followed by the multiplication process. In extracting a root, the same is done except that the division process is used.

**Trigonometrical Functions.** The numerical value of  $\sin a$  and  $\tan a$  may be obtained by means of the scales 'S' and 'T' respectively. The scale of sines 'S' corresponds with the scale  $O_1$ , so that the values of the sines of the angles 'S' are found on the scale  $O_1$  and conversely. Similarly the scale 'T' corresponds with the scale  $U_1$ . Cosines and co-tangents may also be determined from the relation  $\cos a = \sin(90^\circ - a)$ , the complement of  $a$  being calculated mentally, and  $\cotan a = \frac{1}{\tan a}$ .

The slide rule can be made into a trigonometrical table from which the value of the sines and tangents of all angles can be read off with one setting. This is accomplished by drawing the slider completely out and replacing it in the reversed position, so that the scales S, T, and L are now on the front of the rule, with S alongside  $O_1$  and T alongside  $U_1$ . The initial marks of these scales are brought into coincidence. With the slider in this position the

value of the sine of any angle on the scale 'S' can be read off on  $O_1$ , and the values of the tangents of angles on T can be read off on  $U_1$ , and conversely.

**More Accurate Slide Rules.** By increasing the length of the rule increased accuracy can be obtained. A very long rule would be inconvenient to use in practice, so the rule and slide are replaced by two cylinders with the graduations worked along a spiral. Fuller's rule is of this kind and is equivalent to a straight rule 83 feet 4 inches long, so that it is capable of giving results to 1 in 50,000. Fuller's slide rule, or Barnard's modification, are made in spiral form. In addition to its value for multiplication, division, proportion, continuous fractions, roots, and logarithms, it may be used for the determination of natural and logarithmic values of trigonometrical functions of any angle. The products, quotients, &c., of these functions by lengths or numbers, integral or fractional, are obtainable also with ease and precision.

**Combined Slide Rule and Nomograph.** Fig 14 (IV) shows a combined slide rule and nomograph devised by McMullen.<sup>1</sup> Any number on the scale B may be raised to any exponent E by laying a straight edge from the number through the exponent to the A1 scale on which the result will be

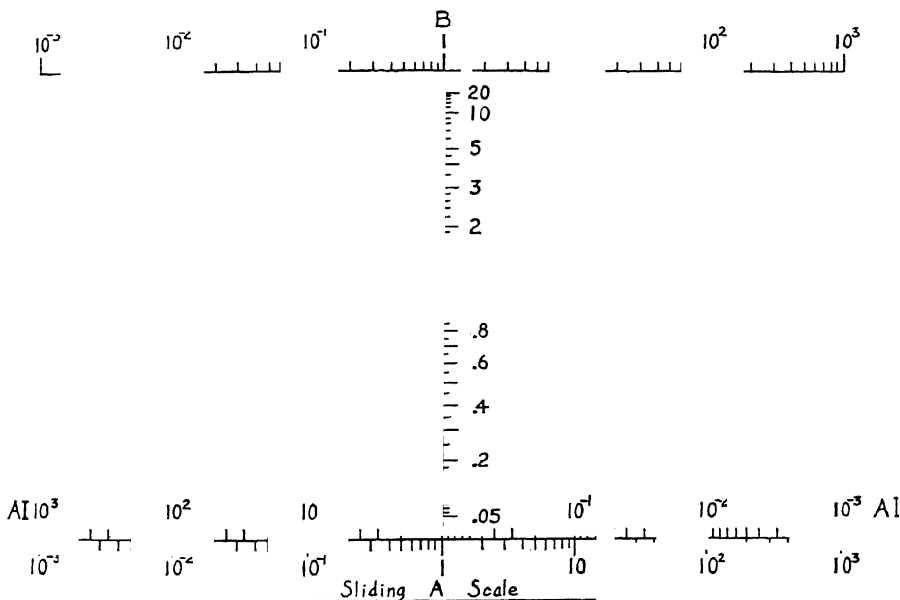


FIG. 14 (IV)

found. To multiply this result by another number, set the second number on the sliding A scale opposite the first result and read the answer on the A scale opposite the index on the A1 scale. To divide a number by an exponential term, place the number on the A scale opposite the index of the

<sup>1</sup> *Ind. and Eng. Chem.*, 1938, 30, 73; see also previous section.

A1 scale, and the result will be found on the A scale opposite the value of the exponential term on the A1 scale. Accumulation of results of successive multiplications or divisions by exponential terms will be found on A scale. When dealing with numbers always larger than unity McMullen states that a Z form or chart may be more useful. However, when accuracy greater than that obtainable with an ordinary slide rule is required it is usual to use logarithms. In making calculations where the possible degree of accuracy is known, the number of figures used should not be greater than is necessary. If a result is known not to be more accurate than 1 in 1,000, it is sufficient to retain four figures in the calculations—if there is any doubt about the accuracy five figures may be used. When the calculations are made by means of logarithms the same fact should be borne in mind: the error in four-figure logarithms does not exceed 1 part in 3,000, and in five-figure logs 1 in 30,000.

## SECTION 4: GRAPHICAL METHODS

One of the commonest procedures in observational science is the plotting of data, obtained from experiments, usually on rectangular co-ordinates. The result of such plotting gives an easily grasped picture of the relation between the factors involved and is a ready, if somewhat rough, method of summarizing the results. At the risk of treading familiar ground a brief account follows of the mathematical concepts underlying the production of such graphs and diagrams.

**Rectangular Co-ordinates.** Two perpendicular straight lines  $X'OX$  (horizontal) and  $Y'OY$  (vertical), intersecting at  $O$ , having been drawn in a plane, it is possible to describe the location of any point,  $P$ , in the plane with reference to these *axes*.  $PM$  is drawn perpendicular to  $X'X$ , cutting it at  $M$ , and  $PN$  perpendicular to  $Y'Y$ , meeting it at  $N$  (see Fig. 15 (IV) ). A know-

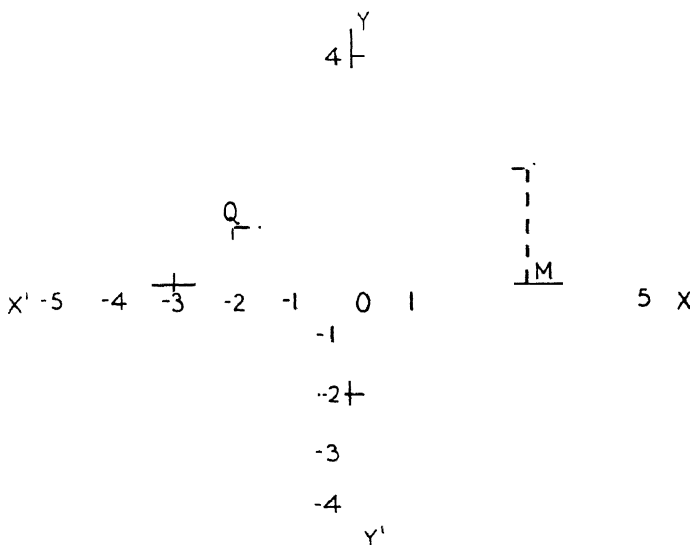


FIG. 15 (IV)  
Rectangular Co-ordinates

ledge of the lengths of  $PN$  ( $= OM$ ) and of  $PM$  ( $= ON$ ) makes it possible to determine the position of  $P$ . The unit of measurement in the direction of each axis having been settled, if  $OM = x$  units and  $ON = y$  units,  $x$  and  $y$  are called the *co-ordinates* of  $P$ . The distance  $x$  along the line  $X'X$  is termed the *abscissa* of the point  $P$ , while  $y$ , the distance along  $Y'Y$  is called its *ordinate*. It is conventional to designate as positive abscissae laid off to the right of the



*origin*, O, and as negative those to the left, while ordinates above the origin are taken as positive and those below negative.

In Fig. 15 (IV)  $OM = 3$  and  $ON = 2$ , thus the abscissa of P is 3 and its ordinate 2. It is a rule of notation always to give the abscissa first, followed by the ordinate, and consequently we write  $P \equiv (3, 2)$ . Similarly  $Q \equiv (-2, 1)$ ,  $R \equiv (-3, -2)$ ,  $S \equiv (2, -3)$ ,  $M \equiv (3, 0)$  and  $O \equiv (0, 0)$ .

It is thus obvious how to determine any point when given its co-ordinates, or how to perform the converse operation of finding the co-ordinates when given the point. In theoretical work it is usual to take the units of measurement on the two axes the same, but in practical charts this is very often inconvenient and it is better to choose such units as will give a diagram of a reasonable size and form. In the location of any point by means of co-ordinates two values are involved; every point ties together and expresses a relation between two factors. Thus if, by any means, a set of measures of two quantities are obtained, linked together in pairs, a diagram may be constructed using the measures of one quantity as abscissae and the corresponding measures of the other as ordinates. A set of points will thus be obtained which will give a picture of the way the two factors are connected and will very often make it possible to obtain an analytical expression for the relationship between them.

**Functions.** When a given mass of gas is enclosed and kept at a constant temperature any variation in the volume is followed by a corresponding variation in the pressure. The two quantities  $p$  and  $v$  which are interdependent are known as *variables*. The fact that  $p$  depends on  $v$  and is uniquely determined for a given mass of gas at a given temperature when  $v$  is known is mathematically expressed by saying that  $p$  is a *function* of  $v$ , and the notation used is  $p = f(v)$ . When  $y = f(x)$  is written the variable  $x$  is called the *independent* variable, while  $y$  is the *dependent* variable. In many cases there is no particular reason why one variable more than another should be taken as independent; the choice of dependent variable depends only on the series of experiments being performed. In any equation in which the time is involved it is, of course, natural to take it as the independent variable. When, therefore, a functional relationship exists between two variables and its expression is known, by arbitrarily assigning values to the independent variables the corresponding values of the dependent variable may be obtained. These pairs of values when plotted with respect to suitable axes give a series of points through which a straight or curved line may usually be drawn, thus providing a 'picture' or graph of the function. The independent variable is always taken as abscissa, i.e. along the  $x$ -axis, while the dependent variable is plotted on the  $y$ -axis.

The most usual types of functional relationships which occur in physico-chemical work are (a) *linear*, (b) *parabolic* or *hyperbolic*, (c) *exponential*, (d) *trigonometric*.

(a) **Linear Curves.** Every relationship of the first degree between two variables gives a straight-line graph. If the equation connecting  $x$  and  $y$  be written in the form  $y = mx + c$ ,  $m$  is a constant representing the slope of the line, that is the tangent of the angle which it makes with the horizontal, while  $c$  is the constant distance from the origin at which the line cuts the  $y$ -axis.

The analytical expression of *Charles's Law* connecting the volume and temperature of a given mass of gas at constant pressure gives a straight-line graph. Thus if  $v_0$  is the volume at  $0^\circ$ , and  $v$  the volume at  $\theta^\circ$ , the analytical expression of the law is  $v = v_0(1 + \theta/273)$ .  $\theta$ , the independent variable,

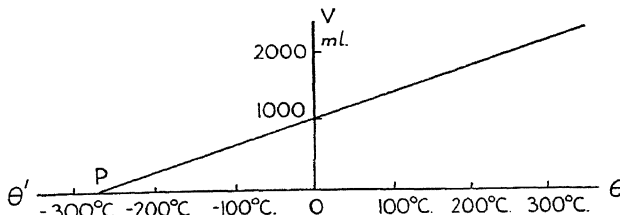


FIG. 16 (IV)

Graph of  $v = 1,000(1 + \theta/273)$

is graphed along the horizontal axis,  $v$ , the dependent variable, is plotted along the vertical axis and Fig. 16 (IV) represents the graph of this equation, when  $v_0 = 1,000$  ml. The point P where the graph cuts the horizontal axis is  $\theta = -273^\circ$ , the absolute zero.

(b) **Parabolic or Hyperbolic Curves.** Non-linear functions are of many kinds, of which it is possible to mention only a few. An equation of the type  $y = ax^n$  gives a parabolic curve when  $n$  is positive ( $\neq +1$ ) and a hyperbolic curve when  $n$  is negative. A case that frequently arises in practice is when  $y$  is expressed as a series of powers of  $x$ ,

$$y = a_0 + a_1x + a_2x^2 + \dots$$

It would be impossible to examine here all the different curves of this type which occur, when the coefficients  $a_0, a_1, \dots$  have different sets of values. However, when, in any particular case, the coefficients are known, little difficulty will arise in drawing the corresponding graph. Very often it happens that the coefficients of the higher powers of  $x$  decrease rapidly, so that  $a_2$  is very small with respect to  $a_1$ , while  $a_3, a_4, \dots$  are quite negligible in comparison. Thus, for instance, the coefficient of cubical expansion for mercury is  $\alpha = 1.8 \times 10^{-4}$ , so that if  $v_0$  and  $\rho_0$  be the volume and density of a given mass of the substance at  $0^\circ$  and  $v$  and  $\rho$  the corresponding volume and density at  $\theta^\circ$ ,  $v = v_0(1 + \alpha\theta)$ . Then

$$\rho/\rho_0 = v_0/v = (1 + \alpha\theta)^{-1} = 1 - 1.8 \times 10^{-4}\theta + 3.24 \times 10^{-8}\theta^2$$

The higher powers in this equation, for ordinary values of  $\theta$ , have little effect on the  $(\theta, \rho)$  graph which differs only slightly from the line

$$\rho = \rho_0(1 - 1.8 \times 10^{-4}\theta)$$

As an example of a curve of the type  $y = ax^n$ , take the equation  $p = RTv^{-1}$  (i.e.  $n = -1$ ,  $a = RT$ ), connecting the pressure and volume of a given mass of gas at constant temperature.  $v$  is taken as the independent variable,  $p$  as the dependent variable and the graphs are drawn corresponding to  $T = 0^\circ$ , and  $200^\circ$  for that mass of gas which occupies 1 litre at N.T.P. Thus  $v = 1$  litre,  $p = 760$  m.m.,  $T = 273^\circ$  K. and hence  $R = 2.784$ , so that, with the litre and millimetre as units, the graphs in question are (a)  $T = 0^\circ$ ,

$pv = 760$ , (b)  $T = 200^\circ$ ,  $pv = 1,317$ . These graphs are drawn in Fig. 17 (IV).

Such a graphical representation of data by means of rectangular co-ordinates has many uses, but for some purposes it is desirable to plot the logarithms of the numbers in question rather than the numbers themselves. This may result in bringing out significant relations more distinctly, or it may serve greatly to simplify and facilitate the manipulation of data. In particular when it is possible, through use of logarithms, to reduce a complex curve to the straight line form a distinct gain has been made in the direction of simplicity of treatment and interpretation. Such will be the case if, in

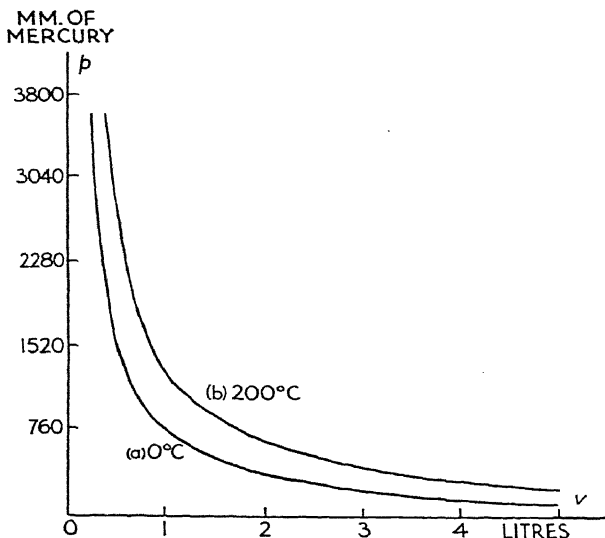


FIG. 17 (IV)  
Graph of  $p = RTv^{-1}$  with  $R = 2.784$ , (a)  $T = 273^\circ \text{K.}$ , (b)  $T = 473^\circ \text{K.}$

the case of the curves plotted in Fig. 17 (IV), the method of plotting logarithms is used. The equations to be plotted are

$$(a) p = 760v^{-1}, (b) p = 2.784 \times 473v^{-1} = 1,317v^{-1}$$

or on reduction to the logarithmic form

$$(a) \log p = 2.88 - \log v, (b) \log p = 3.12 - \log v$$

where the logarithms are taken to two places of decimals. The equations are now *linear in the variables  $\log v$  and  $\log p$* , and when plotted as on Fig. 18 (IV) they give straight-line graphs. On both the axis of  $\log v$  and of  $\log p$  each scale division is taken as representing  $\log 4 = 0.60206$ , while on the same diagram, to indicate the relations involved, the natural numbers corresponding to the logarithms are given in scales to the right and at the top of the figure. It should also be noticed that the origin now corresponds to the point at which  $\log v = 0$ ,  $\log p = 0$ , or  $v = 1$ ,  $p = 1$ , and that quanti-

ties with negative logarithms, i.e. quantities between zero and unity, appear in the diagram to the left of the origin and below it, while, of course, the logarithms of negative quantities cannot occur at all.

It may also be noted that when, as in Fig. 18 (IV), the logarithms in the scales constitute an arithmetic sequence the corresponding natural numbers constitute a geometric sequence, of which the common ratio is the number whose logarithm is represented by one scale division on the log scale.

Clearly any equation of the type  $y = ax^n$  gives, when plotted in similar

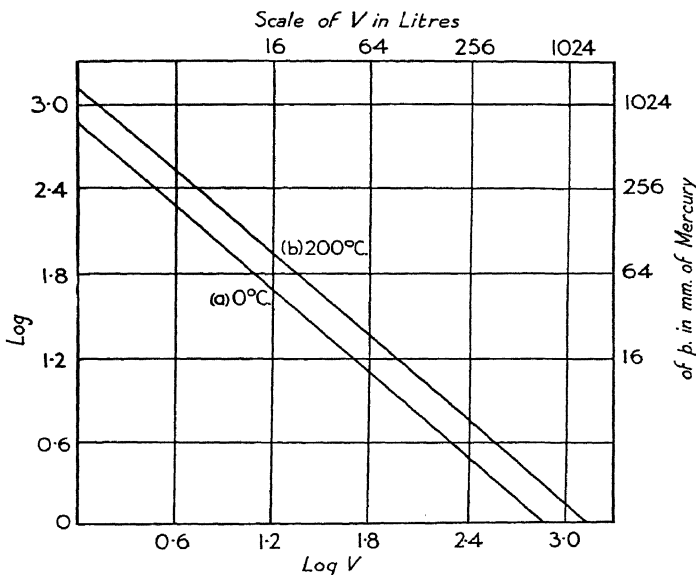


FIG. 18 (IV)

Graphs of (a)  $\log p + \log v = 2.88$   
(b)  $\log p + \log v = 3.12$  [Logarithmic forms of equations (a)  $pv = 760$ , (b)  $pv = 1,317$ ]

fashion, a straight-line graph. On conversion to the logarithmic form the equation of the curve becomes

$$\log y = \log a + n \log x$$

which is obviously linear in the variables  $\log y$  and  $\log x$ .

There are certain disadvantages, however, in plotting logarithms. If a considerable number of points are being plotted the task of looking up the logarithms may be tedious, and, in addition, the original values in which the chief interest is centred do not usually appear on the scale at all. These difficulties may be avoided by constructing graphs on specially prepared paper on which the scales are laid off logarithmically but on which the natural numbers appear. This is an arrangement identical with that employed in the construction of slide-rules. In Fig. 19 (IV) the same graphs, which were plotted in Figs. 3 and 4, are again drawn, but this time on the specially prepared log-log paper. The distance on the scales between

the divisions marked 10 and 20 represents the difference between  $\log 20$  and  $\log 10$ , i.e.  $\log 2$ , and thus is equal to  $\log 40 - \log 20$  or  $\log 80 - \log 40$ , and so on. Consequently since, as may readily be seen by measurement, equal distances on the scales separate 10 from 20, 20 from 40, 40 from 80, this confirms the fact that the axes are scaled logarithmically. The graphs are drawn as before and are shown in Fig. 19 (IV).

If, on such paper as is illustrated in Fig. 19 (IV), it is desired to extend the

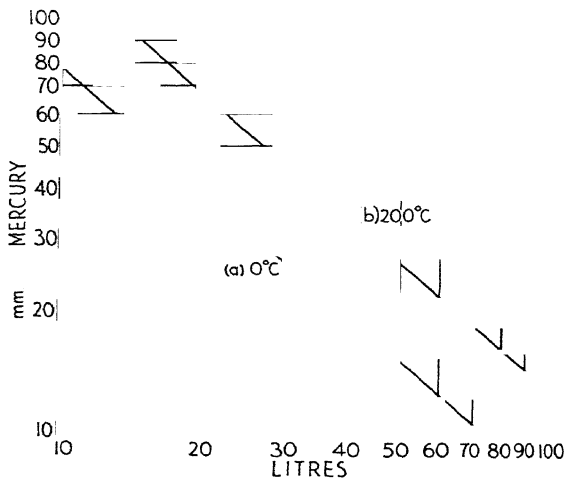


FIG. 19 (IV)

Graphs of (a)  $\rho r = 760$ , (b)  $\rho r = 1,317$  (plotted on paper with logarithmic scales)

scales further in either direction it may readily be done by noting that  $\log 20 - \log 10 = \log 2 - \log 1 = \log 200 - \log 100$ ,  $\log 30 - \log 20 = \log 3 - \log 2 = \log 300 - \log 200$ , &c. Thus the same distances on the scale separate the divisions 1, 2, 3, . . . 10 as separate the corresponding divisions 10, 20, 30, . . . 100 or 1,000, 2,000, 3,000 . . . 10,000, and so on, and, consequently, the part of the scale shown in Fig. 19 (IV) may be extended to include the range from 1 to 100 as illustrated on the vertical scale in Fig. 21 (IV), by duplicating the scale and numbering corresponding divisions as shown.

(c) **Exponential Curves.** Curves represented by equations of the type  $y = ab^x$  are known as *exponential curves*, for in such an equation one of the variable quantities occurs as an index or exponent. It very often happens that the constant  $b$  which occurs in such an equation is equal to the number known as  $e$  ( $= 2.71828 \dots$ ), the base of the natural logarithms. If, for example, it is known that the rate of change of a quantity is proportional to the value of the quantity, that is if  $dy/dt = ky$ , then  $y = Ce^{kt}$  and an exponential curve is obtained.

An illustration of such a curve is got by considering the equation  $J = J_0 e^{-\frac{Rt}{L}}$  which gives the current in a circuit, containing a resistance  $R$ ,

and self-induction with coefficient  $L$ ,  $t$  seconds after the removal of the E.M.F. Take  $R = 0.32$  ohm,  $J_0 = 50$  amps. and  $L = 0.005$  henry, and the equation becomes  $J = 50e^{-64t}$ . This equation is plotted in Fig. 20 (IV) for values of  $t$  between 0 and 0.05 seconds.

The problem presented by the attempt to graph on logarithmic paper such an equation is different to that presented by the equations plotted in

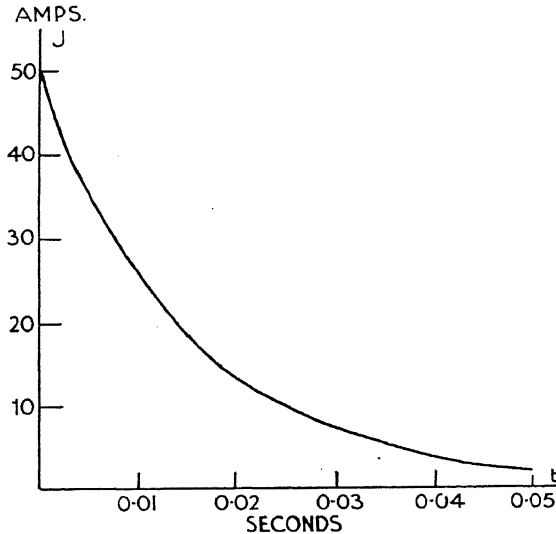


FIG. 20 (IV)

Graph  $J = 50e^{-64t}$

Fig. 19 (IV). Here, on putting the equation into logarithmic form, it becomes

$$\begin{aligned}\log J &= \log 50 - 64 \log e \cdot t \\ &= 1.699 - 27.795t\end{aligned}$$

which is linear in the variables  $t$  and  $\log J$ . If, therefore, the natural  $t$ 's are plotted on the horizontal axis and  $\log J$  on the vertical, a straight-line graph will be obtained. Such a graph may be plotted on specially prepared paper scaled logarithmically on the vertical axis and naturally on the horizontal axis as in Fig. 21 (IV).

(d) **Trigonometric Curves.** The importance of the curve  $y = \sin x$  lies in the fact that it is the simplest case of periodic or harmonic motion. The vibration of taut strings, alternating electrical currents and electron motions within the atom are all examples of periodic motion. By combining different sine curves it is possible to build up any kind of complex curve.<sup>1</sup> Fig. 22 (IV) represents the graph of  $y = \sin x$  and it may be noted that as

<sup>1</sup> See, for example, Eagle, *A Practical Treatise on Fourier's Theorem and Harmonic Analysis for Physicists and Engineers* (Longmans, 1925), or Carslaw, *Introduction to the Theory of Fourier's Series and Integrals* (Macmillan, 1930).

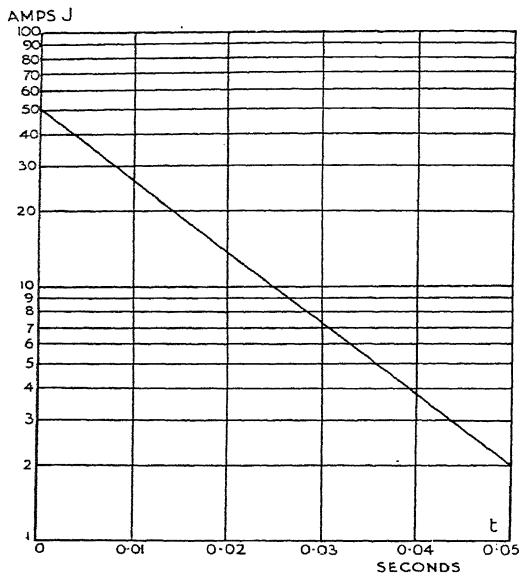


FIG. 21 (IV)

Graph of  $J = 50e^{-7.5t}$  (plotted on semi-logarithmic paper)

$x$  increases  $y$  varies between  $+1$  and  $-1$  and the portion of the curve between  $0^\circ$  and  $360^\circ$  (or 0 and  $2\pi$  radians) is indefinitely repeated, the whole curve consisting of a series of alternate crests and troughs.

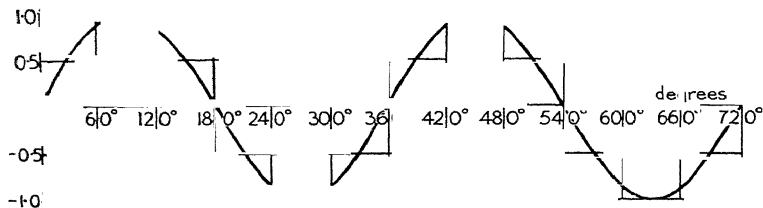


FIG. 22 (IV)

Graph of  $y = \sin x$ 

### Graphical Interpolation and the Finding of Empirical Equations.

When it is known that two given quantities are connected by some mathematical equation it may often be necessary to obtain the values of the dependent variable for a large number of different values of the independent variable. When only a reasonable amount of accuracy is needed in such calculations it is often of advantage to graph the variables in question on suitable scales. A certain number of corresponding points on the graph are

obtained and a smooth curve is drawn through them. [As an aid in drawing the curve, various devices are used ; when the curvature is small a stout ruler is useful ; when it is larger a thin lath of wood can be used. Thin strips of steel are also utilized for the same purpose : in order to keep them bent to the required form they are sometimes backed with a sheet of lead or are fixed to movable metal or wooden arms stiffly jointed together. The strip is placed on a sheet of paper and its curvature altered until it seems to fit best to the marked points, when the curve can be drawn along the edge of the strip. Another convenient device is a French curve which is a piece of celluloid cut with various curved edges so that part of the edge will give a smooth curve through the plotted points.] When the curve has been drawn, the values of either variable corresponding to any values of the other intermediate between the plotted points may be read off.

Very often when a number of corresponding measurements of two factors are obtained from experiment and the points they give are plotted it is found that they lie almost but not exactly on some smooth curve. As a general, though not universal, rule natural phenomena are represented by smooth curves and, consequently, a curve drawn so as to lie evenly among the plotted points will represent the true relation more closely than would the broken line which actually connects the points in question. Having located the 'average' curve which lies most evenly between the points, the deviations of the plotted points from this curve will give some idea of the precision of the results. If they lie close to the smoothed curve the measurements may usually be considered fairly accurate, and the greater the deviation the greater the inaccuracy. The curve found gives a ready picture of the relation between the factors measured and is the first step in determining the mathematical equations which will express the results. If the form of the equation is known beforehand the constants may be evaluated by taking a sufficient number of corresponding points on the smoothed curve and solving the resultant simultaneous equations for the unknown constants in the equation of the curve.

Thus any two points will give the constants if the curve is a straight line, three points will determine  $a_0$ ,  $a_1$  and  $a_2$  if the curve is  $y = a_0 + a_1x + a_2x^2$ , and so on.

When the form of the equation is unknown the first thing to do is to plot the points on ordinary squared paper and so see if a straight line  $y = a_0 + a_1x$  or a parabola of the second ( $y = a_0 + a_1x + a_2x^2$ ), third or higher order would suitably represent the 'average' curve. If this is so the constants may be determined as already explained though probably a better way of evaluating them is to use the Method of Least Squares (see Section 1 of this chapter). Failing a parabola, or indeed in many physico-chemical phenomena before it is tried, one variable should be plotted against the logarithm of the other, using, if available, semi-logarithmic paper of the type already described. If the smoothed curve on this graph is a straight line the relation between the quantities is of the form  $y = ab^x$  and  $a$  and  $b$  may be evaluated by determining the equation of the straight line on the semi-logarithmic paper. If the line on the semi-logarithm graph is not straight, a further choice is to apply the equation  $\log y = a_0 + a_1x + a_2x^2$  to it. Other methods of ascertaining the relationship, by reducing the graph



to the straight line form, are got by graphing  $\log y$  against  $\log x$  (i.e. by using log-log paper where a straight line will mean that the relationship has the form  $y = ax^n$ ), by graphing one variable against the reciprocal of the other or by plotting the reciprocals of the independent variable on the natural scale of the semi-log paper with the logarithm of the dependent variable.

While no general rules can be laid down which will infallibly obtain the 'correct' empirical equation from a set of data it must be remembered that a given set is consistent with any one of a great number of different equations, and that of these the simplest one is chosen.

**Standard Rules for Graphic Presentation.** Graphic methods have been widely employed in many fields and there has been little uniformity in practice. However, the following general rules should, as far as possible, be observed.<sup>1</sup>

1. The general arrangement of the diagram should proceed from left to right, the horizontal scale reading from left to right and the vertical one from bottom to top.
2. Scales should be selected such that the whole of the available space on the chart is efficiently utilized.
3. Whenever possible the zero line of the vertical scale should appear in the diagram and the zero lines, when they appear, should be sharply distinguished from the other co-ordinate lines. The same remark applies to the 100 per cent line when the curves have a scale representing percentages.
4. The curve lines should be sharply distinguished from the ruling.
5. It is inadvisable to show more co-ordinate lines than are necessary to guide the eye in reading the graph; sometimes no guide lines are necessary at all beyond the co-ordinate axes.
6. When curves are drawn on a logarithmic scale the limiting lines of the diagram should each be at some power of 10 on the scales (see Figs. 19 (IV) and 21 (IV)).
7. Figures on the scales should be placed to the left and at the bottom of the diagram or preferably along their respective axes, while all figures and lettering in the diagram should be so placed as to be readily legible from the bottom or right hand edge of the diagram.
8. In curves representing a series of observations the points representing the separate observations should as far as possible be indicated clearly on the diagram.
9. It is desirable that in most cases numerical data should be available in a table accompanying the diagram.
10. The title of the diagram should be as clear and as complete as possible.

<sup>1</sup> See *Quarterly Publication of the American Statistical Association*, 1915, 14, 790-7.

## CHAPTER V

### PHASES

#### SECTION 1: THE PHASE RULE

**T**HE Phase Rule of Willard Gibbs can be stated in the form of the equation

$$P + F = C + 2$$

where  $P$  = the number of phases, solid, liquid or gaseous

$F$  = the number of degrees of freedom (temperature, vapour pressure, concentration), and

$C$  = the number of components

It must be recalled that the Phase Rule can only be applied to systems which are in equilibrium.

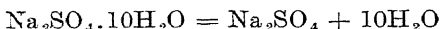
In the case of one component systems such as, for example, water, since  $C = 1$ ,  $P + F = 3$ . If then there are two phases, such as liquid water and vapour,  $P = 2$  and so  $F = 1$ ; there is one degree of freedom, or the system is univariant. The system is therefore completely defined if one fixes any one of the three variables, namely, either the temperature, the pressure, or what comes to the same thing, the concentration of the vapour: one variable having been fixed, the others become automatically fixed; thus if we fix the temperature the vapour pressure is fixed, as we know from the fact that we have tables giving the vapour pressure corresponding to any temperature.

Should there be three phases,  $P = 3$  and so  $F = 0$ . The system has no degrees of freedom, it is non-variant and is already defined; thus in the case of water if we have the three phases, solid ice, liquid water, and vapour, in equilibrium the system is already definite because it can only remain in equilibrium at a temperature  $+ 0.008^{\circ}$  and a pressure of 4.6 mm. of mercury. This point is the so-called triple point of the system.

**Nature of Transition-point.** Certain substances are capable of existing in more than one crystalline form and are then said to be polymorphous. In some cases either one form of the substance can be converted into the other and then the substance is said to be enantiotropic. When the two forms are not reversibly convertible the substance is said to be monotropic. A well-known case of enantiomorphism is that of sulphur. At the room temperature monoclinic and rhombic crystals of sulphur can be prepared, but it is found that the rhombic crystals are stable, while the monoclinic are unstable and lose their transparency in a day or two, owing to their changing over into the rhombic form. The two forms have different

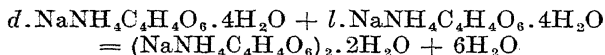
physical properties ; for example, the monoclinic (being the unstable form) has the greater solubility and greater vapour pressure. At temperatures above  $95.5^{\circ}$  the opposite conditions hold, the monoclinic being the stable form and the rhombic the unstable ; the latter will therefore have the greater solubility and vapour pressure. There exists one temperature, called the transition temperature, at which both forms are stable and can coexist, and it follows that at this temperature ( $95.5^{\circ}$  in the case of sulphur) the solubilities and vapour pressures are the same for both forms. The transition temperature may be compared with the melting-point of a pure substance—it is just as definite and has been used by Richards as a fixed point in thermometry ; it is lowered by the addition of a foreign substance, and this lowering has been used to determine the molecular weight of the foreign substance. Transition-points are found in the case of elements, such as sulphur, iron, and tin, and with compounds such as ammonium nitrate, mercuric iodide and potassium nitrate. In addition to these cases there are a large number of similar ones with the crystalline hydrates of salts.

*Example.* The transition-point of the system



may be taken as an example. When a hot saturated solution of sodium sulphate is evaporated at temperatures above  $33^{\circ}$ , the solid which separates is the anhydrous salt ; at temperatures below  $33^{\circ}$  crystals of the decahydrate are obtained. Again, if a saturated solution of the anhydrous salt is prepared above  $33^{\circ}$  and excess of the anhydrous salt is added, on cooling below  $33^{\circ}$ , the solid phase will change over to the decahydrate. When the decahydrate is heated alone it appears to melt at  $33^{\circ}$ , the decahydrate solid is transformed into the anhydrous salt and water, the amount of water produced being just sufficient to dissolve the anhydrous salt. In this case the solubility of the anhydrous salt decreases with rise of temperature so that on heating above  $33^{\circ}$  anhydrous salt separates out from the solution.

Another example is the system—Sodium ammonium tartrate tetrahydrate to sodium ammonium racemate dihydrate



Solutions of this salt, when crystallized below  $28.3^{\circ}$ , give a mixture of the dextro- and laevo-tartrate crystals. Above the transition temperature crystals of the racemate are obtained.

#### ONE COMPONENT SYSTEMS

We may take as an example the case of sulphur where we can make use of the difference in the specific gravity of the two forms. Monoclinic sulphur is less dense and so has a larger specific volume than the rhombic form ; if therefore a mixture of the two forms is held at a temperature just above the transition point there will be a steady but slow increase in volume as the rhombic changes over into the more bulky monoclinic ; conversely below  $96^{\circ}$  there will be a decrease in the volume due to the opposite change. A mixture of the two forms is used because if one form only is present there

is not unfrequently some delay in the formation of the first traces of the second form.

**The Dilatometer Method.** (See also Chapter XII (I) on the Determination of Transition Points.) A diagram of the apparatus is shown in Fig. 1 (V). The cylindrical bulb has a capacity of about 40 ml. and to this is sealed a capillary tube B of 0.5 cm. bore and a wider tube C. The dilatometer is filled by inverting it and dropping in a glass bead to close the entrance to the capillary: the solid is introduced through the tube C, which is then sealed. After it has cooled, the dilatometer is inverted and filled with a suitable liquid; it is an advantage if the solid is slightly soluble in the liquid, but of course the liquid must not dissolve in the substance under examination since this would lower the transition temperature. The top of the capillary B is passed through the cork in an adapter and the liquid to be used is placed in the latter. The adapter is attached to the pump and the air is removed from A as completely as possible; on releasing the pressure the liquid in the adapter is forced down into A. The process is continued until all air bubbles have been removed and the meniscus of the liquid is in B. The meniscus is then brought near the bottom of B by passing a fine-drawn-out capillary of glass down the bore. A millimeter scale is wired on to the tube B.

It is convenient to use an electrically heated oil-bath as the thermostat. The vessel which contains the paraffin oil is a cylindrical beaker about 10 cm. in diameter and 25 cm. high; this stands in a slightly larger beaker and the space between the two is packed with felt or some other non-conducting material. The heater consists of a framework having at the top and bottom fireclay rings with grooves to prevent the wire from slipping: the rings are maintained in position by vertical strips of brass. Over the frame is wound about 10 metres of No. 24 S.W.G. constantan wire, so that the resistance is about 25 ohms; if a 110-volt circuit is used for the heating, a regulating rheostat of about 80 ohms is necessary so that the current can be cut down to 1 amp. A key for making and breaking the current will be used. The oil can be stirred very conveniently by bubbling a stream of air, obtained from the water-pump or otherwise, through a glass tube which reaches to the bottom of the vessel. A thermometer reading to  $100^{\circ}$  in  $0.1^{\circ}$  is fixed in a stand so that its bulb is near the centre of the dilatometer bulb and a short stem thermometer reading up to  $60^{\circ}$  is fixed so that its bulb is half-way between the surface of the oil and the  $96^{\circ}$  mark on the first thermometer; this is for the exposed thread correction.

Fill the dilatometer with powdered roll sulphur as described above and seal the tube C: when cool, invert and fill with xylene, which is a suitable liquid on account of its high boiling-point and its solvent action on sulphur. Adjust the meniscus, affix the scale and place the dilatometer in position in the thermostat so that the bulb is well immersed. Start the heating and raise the temperature to  $100^{\circ}$  and maintain it there; this will give practise in regulating the temperature, which is done partly by the use of

B

/ \

FIG. 1 (V)

the key and partly with the regulating rheostat ; after a time the latter will be the chief means and the key will be used only occasionally.

The apparatus is to be maintained at  $100^{\circ}$  for some time to allow a fair amount of rhombic to go over into monoclinic sulphur. This can be followed quite readily because when the dilatometer is exposed, for example, to a rise of temperature, there will be the change in volume, due to the expansion of the glass, of the sulphur and of the xylene ; this will be complete in from 3 to 5 minutes, and will be followed by a slow continuous change of rhombic into monoclinic, giving an increase in volume if we are above the transition temperature as we are in this case, or if we were below the transition-point there would be a continuous decrease in volume due to the reverse change. At this stage it may be necessary to remove some of the xylene with the aid of the thin glass capillary.

When you are satisfied that a reasonable amount of monoclinic sulphur has been formed, lower the temperature to  $98^{\circ}$  and keep it there for 10 minutes : there will be a decrease in volume during the first 3 to 5 minutes due to contraction of dilatometer, sulphur, and xylene, and then a slow rise due to the continuance of the change of rhombic crystals into monoclinic. Repeat in turn at  $97^{\circ}$ ,  $96^{\circ}$ ,  $95^{\circ}$ ,  $94^{\circ}$ , &c. In this way you will reach a temperature where the first decrease in volume is followed, not by an increase, but by a slow decrease showing that now monoclinic sulphur is passing over into rhombic. If this happened at  $94^{\circ}$  you would know that the transition point was between  $94^{\circ}$  and  $95^{\circ}$ . The point may be fixed more exactly in the following way : the rate at which one form passes over into the other will be roughly proportional to the difference in vapour pressure of the two forms ; this is zero at the transition point and increases as the temperature becomes removed from the transition point ; suppose then that at  $94^{\circ}$  the meniscus falls in the second stage over two scale divisions in 5 minutes and at  $95^{\circ}$  rises over three scale divisions in 5 minutes ; then the last temperature is farther from the transition point in the ratio of three to two, i.e. the transition-point is  $94.4^{\circ}$ .

Finally, to the temperature so obtained, apply the correction for the exposed thread of the thermometer and so get the corrected temperature of the transition. (Compare with Reicher's results given later.)

**Liquid Crystals.** A very interesting case of a one-component system is that of the so-called liquid crystals first observed by Reinitzer in the case of cholesteryl acetate and benzoate. *p*-Azoxyanisole and *p*-azoxyphenetole show the phenomenon particularly well. These substances melt sharply at a definite temperature to form a milky liquid, and this on further heating suddenly clears, also at a definite temperature, e.g. with *p*-azoxyanisole the first change occurs at  $118.27^{\circ}$  and the second at  $135.85^{\circ}$ . On cooling, the changes take place in the reverse order. The milky liquids are anisotropic, they show double refraction and give interference colours when examined by polarized light : it was because these properties had previously only been observed with crystals that the name liquid crystals was used.

They probably consist of long molecules arranged parallel to one another with only one axis fixed in space.

## TWO COMPONENT SYSTEMS

**Thermal Analysis.** When a pure substance, whether element or compound, is melted and cooled, the solid which separates has the same composition as the liquid which remains. Also, if the temperature of the liquid is taken at regular intervals during the cooling, it will be found that there is a continuous fall as long as the whole mass remains liquid, but that as soon as the solid begins to appear the fall of temperature is arrested and the temperature remains constant as long as any liquid remains and only recommences to fall when the whole mass has become solid. While the liquid is cooling heat is being lost by radiation, &c., but when the solid begins to separate the latent heat of solidification is set free which balances the heat lost and so prevents the temperature from falling. When all is solid there is no more latent heat available and the temperature again falls. If we plot a cooling curve with temperatures as ordinates and times as abscissae, there will be a horizontal portion corresponding to the period while solidification is occurring.

When a melt containing two components is cooled conditions are more complicated because the solid which first separates may consist of:

- (1) Crystals of one pure component
- (2) A compound
- (3) Mixed crystals, or
- (4) A eutectic mixture

A good deal of information as to what occurs can be obtained by the method of thermal analysis of a series of mixtures of different percentage composition, more particularly if this is completed by a microscopic examination of sections of the resulting solids.

Taking, for example, alloys of two metals such as zinc and cadmium, when the case is as simple as possible (case 1 above). Pure zinc has a melting-point of  $418^{\circ}$ , so that if it is melted and cooled and a temperature-time diagram is constructed, the curve will show a horizontal line at the  $418^{\circ}$  level.

If a mixture of equal parts of zinc and cadmium is melted and allowed to cool, the cadmium lowers the freezing-point of the zinc (just as salt lowers the freezing-point of water) and no solid will appear until the temperature is somewhere about  $320^{\circ}$ , when crystals of pure zinc will begin to separate: latent heat is set free and the rate of cooling is slowed down. The point when crystals begin to separate is indicated by a break in the temperature-time curve, but this time there is no horizontal portion, because the solid separating has a different composition from the melt. The reason for this is that the removal of some of the zinc from the melt makes the latter richer in cadmium, so that the cadmium lowers the freezing-point of the zinc still more and the temperature must fall a little before more zinc crystals can separate. This makes the solution still richer in cadmium; the cooling curve continues downwards then, and the melt continues to grow richer in cadmium.

This process continues till the temperature reaches  $270^{\circ}$ , and the melt contains 82.6 per cent of cadmium.

The temperature now remains constant at  $270^{\circ}$  till the whole has solidified (cooling curve horizontal) and the zinc and cadmium crystals separate

out side by side in the same proportions as they are in the melt (eutectic mixture). In a similar way a melt containing 90 per cent cadmium would show first a break and then a horizontal portion on the cooling curve: the break would be below the freezing-point of cadmium because the zinc lowers the freezing-point and the solid which separates would consist of crystals of cadmium until the temperature falls to  $270^{\circ}$  and the melt has the composition of the eutectic.

If a mixture is made up to have the composition of the eutectic at the start and is melted and cooled, its cooling curve will resemble that of a pure substance melting at  $270^{\circ}$ .

The method of thermal analysis consists in preparing, by weighing out the two components, a series of mixtures, and then from the first break in the cooling curve, determining the temperature at which solid first begins to separate. These temperatures are then plotted as ordinates against the percentage compositions as abscissae. The form of the resulting curve gives very definite information as to the composition of the solid phase.

The thermocouple forms a convenient and simple method of measuring temperatures which are somewhat too high for the use of the ordinary mercury thermometer. Platinum and platinum-iridium thermo-elements give good results up to  $1200^{\circ}$ , but for lower temperatures copper-constantan is used, because it gives an E.M.F. about forty times as great, namely about 40 microvolts per degree.

The relation between the E.M.F. and temperature is given by such equations as

$$E = m.t^n$$

or

$$E = a + b.t + c.t^2$$

but the values of the constants must be determined experimentally for each thermocouple.

The thermocouple is made of thick wires from 0.1 to 0.2 mm. diameter; the end of the copper wire and that of the constantan are twisted together and soldered together to form the hot junction. On one wire is threaded porcelain or hard glass beads to ensure that contact between the wires is made only at the soldered end, and this is then placed at the bottom of a closed and narrow porcelain tube about 20 cm. long. Each of the free ends of the wires is twisted on to the end of a lead of covered copper, these joints are soldered, a thin glass tube having been placed over one wire before the joint was made is now pushed down near to the joint and this is pushed down into a narrow glass tube. During the experiment the two glass tubes are immersed in ice shavings in a Dewar flask, so that the cold junction is always at  $0^{\circ}$ .

The E.M.F. may be measured by means of the ordinary potentiometer, but it is more usual to use a suitable galvanometer. A pointer galvanometer in which the deflection is nearly proportional to the current, and having a sensitiveness of about  $10^{-7}$  amps. per scale division, and having a resistance of about 400 ohms, is suitable.

The current is proportional to the E.M.F. divided by the total resistance: if the galvanometer resistance is about 400 ohms, and that of the thermocouple about 2 ohms, any changes produced in the resistance of the thermo-

couple by heating will have a negligible effect on the total resistance, and the current will be proportional to the E.M.F.

**Calibration of the Thermocouple.** This is carried out by means of a number of fixed points which define temperature, suitably disposed over the range for which the instrument is to be used. In this case the highest temperature will be about  $460^{\circ}$  and the fixed points are

the melting point of zinc	= $418^{\circ}$
the melting point of cadmium	= $321^{\circ}$
the melting point of tin	= $232^{\circ}$

The problem is to find the scale reading of the galvanometer corresponding to each of these temperatures and then to draw a curve for temperature plotted against scale reading so that other temperatures can be read off from the curve.

The temperatures are found by determining the cooling curve of the melted metal. Starting with the metal tin: about 30 grams are placed in a test-tube made of combustion tubing (or better in a Tamman porcelain crucible 1.5 cm. in diameter and 15 cm. high). A little powdered charcoal is added to form a layer on top of the melted metal and so prevent oxidation by the air. A large fireclay crucible is filled with sand or magnesia and is supported on a tripod and heated with a small bunsen flame so as to keep its temperature round about  $150^{\circ}$  in order that cooling shall not be too rapid. Melt the tin and place the tube containing it in the centre of the sand in the big crucible; place the porcelain tube containing the hot junction of the thermocouple so that it reaches well down into the melted metal but does not touch the sides of the tube containing it, and fix it in position with a clamp and stand.

Take readings of the galvanometer every 15 seconds if possible; it is best for one observer to watch the galvanometer and a second one to indicate the quarter minutes and do the recording. Proceed till the stationary period has been passed and the whole is solid. Next determine whether the galvanometer deflection corresponding to the stationary period ( $232^{\circ}$ ) is suitable, remembering that the highest temperature to be read is about  $460^{\circ}$  and that this temperature should correspond to the extreme limit of the galvanometer scale. If the temperature  $232^{\circ}$  is more than half way over the galvanometer scale it can be brought down by including a resistance in the circuit and the value of this resistance can readily be calculated from the known resistance of the galvanometer.

When this adjustment has been made, remelt the tin and again determine the cooling curve and from this obtain the scale reading of the galvanometer corresponding to  $232^{\circ}$ .

Repeat the experiment in exactly the same way with cadmium, getting the scale reading corresponding to  $321^{\circ}$ , and with zinc that corresponding to  $418^{\circ}$  (in the case of zinc continue the readings to a low temperature; plot the cooling curve and see if you can detect any breaks at  $310^{\circ}$  and  $170^{\circ}$ —these points are transition points between different allotropic forms of zinc but they are not easy to detect owing to the smallness of the heat changes at the transition points). Plot a curve showing the relation between scale reading and temperature.



DETERMINATION OF THE FREEZING-POINT DIAGRAM FOR THE SYSTEM  
CADMIUM-ZINC

The freezing-points of the pure metals have already been determined in terms of the scale readings of the galvanometer. Prepare a series of mixtures having the following proportions of cadmium/zinc: (a) 90/10, (b) 82/18, (c) 70/30, (d) 50/50, (e) 25/75. A total mass of 30 grams of each mixture will be sufficient. Place the first mixture (a) in a Tammann crucible and, after adding some powdered charcoal, melt the alloy and determine the cooling curve in exactly the same way as was done in the case of the pure metal. Plot the scale readings against time on squared paper. You will find a break in the curve at some temperature below the freezing-point of pure cadmium; this is the point at which solid first commences to separate and is to be noted as the freezing-point of the melt having the composition cadmium, zinc = 90/10; after this break the curve will continue to fall as the composition of the liquid changes owing to the deposition of cadmium, until the eutectic point is reached, when the curve will become horizontal; after all has solidified the curve will again fall. This experiment then gives the galvanometer scale readings corresponding to the 90/10 mixture and also that corresponding to the eutectic point. Convert these scale readings to temperatures from the calibration curve already constructed.

Repeat with mixture (b)—actually this has the eutectic composition and the cooling curve will resemble that of a pure substance; a second value for the eutectic temperature is found.

Similarly repeat with mixtures (c), (d) and (e); the results will resemble those for (a), and the freezing-points for the mixtures and additional values for the eutectic point will be obtained. Draw the freezing-point diagram, plotting temperature as ordinates and percentage composition as abscissae and note that the form of the curve is that where pure substances separate and no mixed crystals or compounds are formed. Consult the textbooks to see what the curves are like in these cases.

It is very instructive to prepare sections of (a), (b), and (c) for examination under the microscope. For this purpose the tube containing the alloy is broken and a small section with parallel sides cut with a hacksaw. The specimen is ground with emery paper: first using a coarse paper stretched over a flat surface, grind the disc until the two surfaces are parallel as near as can be judged; then grind one surface with emery paper of gradually increasing fineness and finally polish this surface with moist jeweller's rouge on a piece of chamois leather stretched over a piece of wood. The polishing is complete when no scratches can be seen on the surface when it is examined with a lens. Emery paper is rather apt to chip the surface and it is better to rub the specimen down on a smooth carborundum stone if one is available.

The specimen is placed for a few moments in dilute nitric acid to etch the surface and is washed and dried.

The etched surface is examined under the microscope with vertical illumination. The vertical illuminator is a small attachment behind the objective by means of which light from the side is reflected downwards by means of a prism or piece of plane glass through the objective on to the specimen, from which it is reflected up again into the microscope. The

specimen is placed on the stage, illuminated as described and examined under not too high a power.

In specimen (*a*) cadmium crystals will be seen embedded in the eutectic ; in specimen (*c*) zinc crystals in the eutectic, and in (*b*) the eutectic alone.

#### PARTIALLY MISCIBLE LIQUIDS

**Phenol and Water.** When equal quantities of phenol and water are mixed at the room temperature, the mixture separates into two layers, the upper consisting of a solution of phenol in water and the lower a solution of water in phenol : we therefore have two components and three phases (two liquids and vapour), so the system will have one degree of freedom and at a given temperature the composition of each liquid will be fixed. The solubility of each liquid in the other increases with temperature, so a rise of temperature causes them to approach one another in composition and eventually they will become similar and the two layers will be replaced by a single homogeneous liquid : on cooling this liquid the two layers will reappear at a certain temperature and this is well marked by the sudden appearance of turbidity in the liquid.

The mutual solubility curve can be obtained in the following way. A small boiling-tube is fitted into a larger one by means of a cork and through the stopper of the inner tube pass a thermometer ( $100^{\circ}$ ) and a stirrer. Enough phenol to cover the bulb of the thermometer, about 10 grams, is weighed into the tube and 4 ml. of water, measured accurately from a burette, is added. The inner tube is warmed in boiling water till a homogeneous liquid is obtained, cooled under the tap till it becomes turbid, heated again to clearness, the outside dried and the tube replaced in the jacket. The liquid is then stirred briskly until a permanent turbidity is obtained and the temperature is read. A further 1 ml. of water is added and the experiment repeated, and so on, increasing the total volume of water by steps to 7, 9, and 12 ml. The tube is emptied and the experiment continued with 4 grams of phenol and adding totals of 8, 12, and 16 ml. of water, and finally 2 grams of phenol with 11 and 18 ml. of water. Calculate the percentage of phenol in each mixture and plot these as abscissae against the temperatures of formation of the two phases as ordinates. The critical solution temperature, the highest temperature at which two phases can coexist, is affected by the addition of a third substance in just the same way as the freezing-point of a liquid is lowered by the addition of a solute.

## SECTION 2: THE GRAPHICS OF MULTI-SYSTEMS

In physical chemistry, especially in that portion which deals with the phase rule, it is frequently necessary to represent graphically the composition of systems of three components. For this purpose a triangular diagram is particularly suitable, and the method of applying it is indicated below.

The principle underlying the use of such diagrams depends on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is constant. In general the composition of

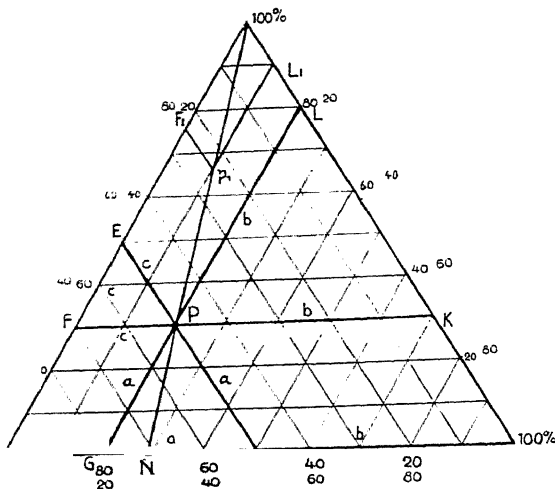


FIG. 2 (V)

any combination of three substances can be represented by a point in or on the triangle. The vertices indicate the single substances, the sides of binary mixtures and ternary mixtures are represented by points within the triangle.

An equilateral triangle (Fig. 2 (V) ) is constructed the sides of which are taken as equal to 100 (or 1 unit), and the sum of the percentage or fractional parts of the components corresponds to a side of the triangle.<sup>1</sup> The vertices ABC represent the three components in the pure state, points on the sides AB, BC, and CA correspond to mixtures of the two components represented by the vertices terminating the side in question. Thus the point D corre-

<sup>1</sup> Messrs. Schleicher and Schüll, Düren, Germany, supply suitable ruled paper for triangular co-ordinate work.

sponds to a mixture of 50 per cent B and 50 per cent C, or 0.5 parts of B and 0.5 parts of C.

To represent a mixture of say  $a$  A,  $b$  B and  $c$  C, where  $a = 30$ ,  $b = 50$ ,  $c = 20$ , BF is made equal to  $a$  and FP is drawn parallel to BC, and the line EP parallel to AC where  $AE = b$ . These lines intersect in a point P, and it is evident from elementary geometrical considerations that PG, PD equal  $a$  where PG, PD are respectively parallel to AB, AC; PK, PL equal  $b$  where these lines are parallel to BC, BA, and PF, PE, which are parallel to CB, CA, equal  $c$ . Further,  $PG + PK + PF$  is equal in length to the side of the triangle.<sup>1</sup>

Thus the percentage of any component in a mixture represented by a point such as P is given by the length of the lines drawn parallel to the two sides of the triangle which meet in the vertex which represents that component in the pure state. Further if a line APN be drawn from one of the vertices A of the triangle to the opposite side, points on this line represent mixtures in which the ratio of the components B and C is constant. This follows from the fact that  $P^1F^1/P^1L^1 = PE/PL = NB/NC$ .

Such lines therefore correspond to the addition of one component to a mixture of the other two.

As an example of the application of the methods in Fig. 3 (V) the line AB gives the composition of all mixtures of *n*-butyl alcohol, acetone, and water which are saturated at a given temperature with respect to one or other of the components water or butyl alcohol, and will separate into two layers if that component is added even in very small quantities. The other lines CD, EF, &c., on the diagram are drawn through mixtures of the same specific gravity, so that the density of any mixture of the three substances in question is at once apparent from the figure. The equilibrium relations between chloroform, acetic acid and water were worked out by Wright.<sup>2</sup>

Five mixtures of chloroform and glacial acetic acid are to be made up in 150-ml. bottles. The total mass of each mixture is to be 50 grams and they are to contain 80, 60, 40, 20, 10 per cent of chloroform respectively. Since the density of chloroform is 1.50 and that of acetic acid 1.05 the corresponding volumes will be

Chloroform	Acetic acid
26.7 ml.	9.5 ml.
20.0 ml.	19.0 ml.
13.4 ml.	28.5 ml.
6.7 ml.	38.0 ml.
3.3 ml.	42.8 ml.

These volumes are measured accurately from a burette and the bottles are placed in a thermostat at 25°. After allowing 20 minutes for temperature equilibrium to be established the contents of each bottle is titrated with water from a burette till the first appearance of turbidity due to the appearance of a second phase. The bottle must be well shaken after each addition of water. In order to avoid overstepping the endpoint it is advisable to withdraw a small fraction of the mixture by means of a pipette before starting the titration: water is then added till turbidity is produced, the

<sup>1</sup> Reilly and Ralph, *Sci. Proc. Roy. Dubl. Soc.*, 1919, 15, 602.

<sup>2</sup> *Proc. Roy. Soc.*, 1891, 49, 174; 1892, 50, 375.

small fraction is returned to the main bulk which causes the liquid to clear up and more water is then added by very small steps. Note that very little water (about 1 ml.) will be required in the richest chloroform mixture. With water and chloroform alone, when sufficient of each is present the

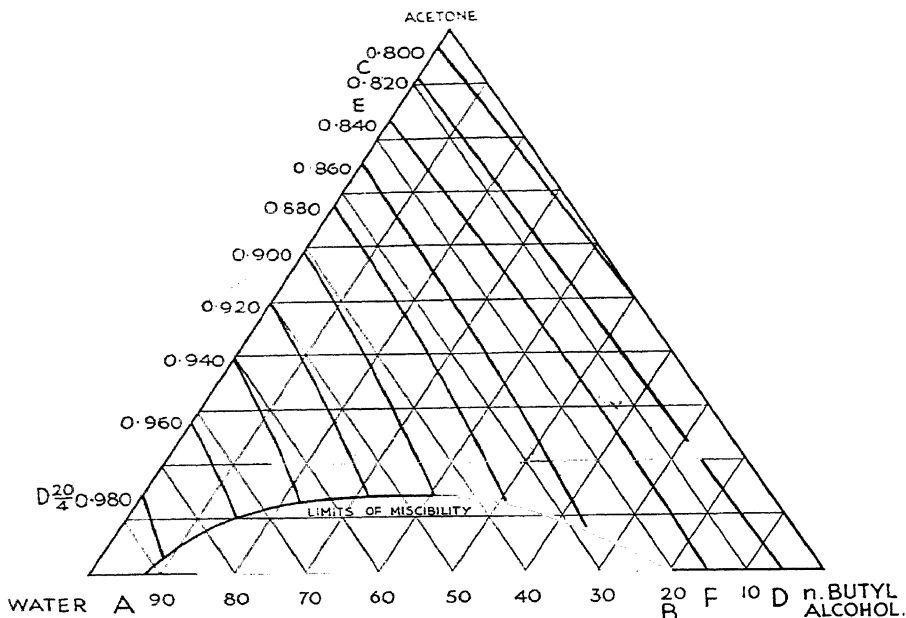


FIG. 3 (V)

composition of the two layers is: heavier layer 99 per cent chloroform, 1 per cent water; lighter layer 0.8 per cent chloroform, 99.2 per cent water. With these figures and those obtained in the experiment the triangular diagram may be drawn.

#### ISOTHERMAL DIAGRAM FOR SALT SOLUTIONS

The method is particularly suitable for the investigation of a system of, for example, two salts and water to find out whether double salts, mixed crystals, or salt hydrates are formed.

Fig. 4 (V) shows the form of the diagram in which a double salt is formed, the composition of this salt being represented by the point D. If this salt had water of crystallization the point D would lie within the triangle, while if one of the single salts, say B, contained water of crystallization, the tie lines would converge to some point on the side of the triangle B-H<sub>2</sub>O and not to B, as they do when the solid phase is the anhydrous salt.

To obtain the diagram, mixtures of the three components in various proportions are made up in bottles and shaken in the thermostat. From

each bottle the saturated solution and a sample of the moist solid are separated and analysed. In one case the composition of the solution might be that represented by the point  $h$  and that of the moist solid by the point  $e$ ; if these two points are joined and produced, the point in which the line cuts the side of the triangle, in this case  $A$ , gives the composition of the dry solid;  $Ae$  being proportional to the amount of solution adhering to an amount  $eh$  of the solid. When the solid is the pure single component, several of these tie lines will intersect in  $A$ .

Similarly, if a double salt  $D$  is formed,  $f$  and  $g$  would represent the composition of two of the moist solids and that of the corresponding saturated solutions would be the points where the tie lines cut the curve  $cc'$ .

If mixed crystals were formed each tie line would go to a separate point

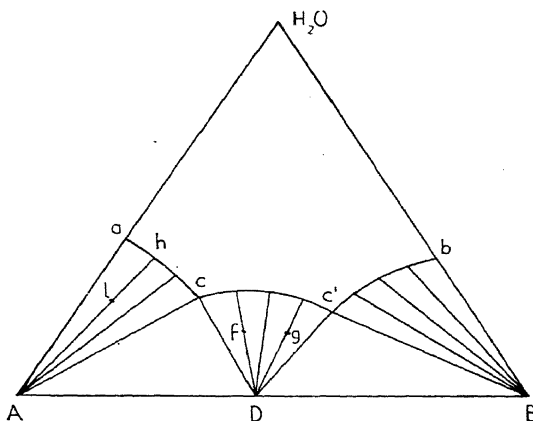


FIG. 4 (V)

on  $AB$ . The method may be examined with the system  $\text{NaCl} - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$  at  $15^\circ$  in which the solids are  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .

A somewhat similar method has been employed by Gibbs, in which an equilateral triangle of unit height is employed. The sum of the concentrations of mixtures of the three components is represented by the height of the triangle, and as before the corners represent the pure substances, and points in the sides give mixtures of the two components. Points within the triangle correspond to mixtures of the three components, and the fraction or percentage of a component present in a mixture is given by the perpendicular distance of the point from the side of the triangle opposite the vertex representing that component. The sum of the perpendiculars from a point within an equilateral triangle on to the sides is of course equal to the height of the triangle.

To fix a point each perpendicular from the three vertices is divided into 10 or 100 parts, and through each division lines are drawn at right angles to the perpendicular (Fig. 5 (V)). The position of any point can then be read off immediately. The point indicated where the three heavy lines

meet, for example, represents a mixture X 30 per cent, Y 20 per cent, and Z 50 per cent.

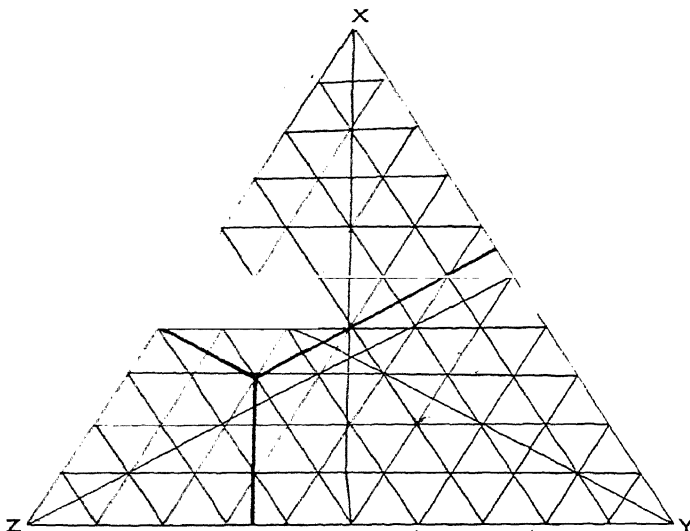


FIG. 5 (V)

**Representation of Temperature.** If it is desired to represent the change of another independent variable such as temperature it is measured along an axis drawn perpendicular to the plane of the triangle; a right prism is thus obtained as a figure of reference. Sections parallel to the base give triangles corresponding to isothermal conditions.

In the chapter on separation of gases by solution (Vol. II, Chap. I\*, S. 5) an account is given of the use of a graphical method in dealing with problems of fractional solution applied to hydrogen and carbon dioxide.

**Four Components.** To represent mixtures of four components a tetrahedron is employed. The principle employed is the same, the vertices correspond to the components, the edges to mixtures of the two components represented by the vertices the edge in question joins, the faces give mixtures of the three of the components indicated by the vertices of the face, and mixtures of the four components are given by points within the figure. Mixtures with a constant ratio of two of the components lie on planes through the edge joining the other two; when the ratio of three of the components is constant, the corresponding mixtures lie on a line through the fourth vertex.

The study of transition changes from the phase-rate standpoint is considered later. The use of freezing-point diagrams also demonstrates a use of cooling curves, as they indicate the temperature at which a change of phase occurs.

## CHAPTER VI

### MISCELLANEOUS APPARATUS

#### SECTION 1: THERMOSTATS

**I**NTRODUCTION. Changes in temperature affect the value of most physical and chemical constants so that it is necessary to carry out the determination of such constants at a fixed temperature. This is usually accomplished by immersing the apparatus employed in a bath of liquid kept at a steady known temperature. Such a bath is called a thermostat.

At a few degrees above room temperature it is possible to maintain the temperature of a thermostat constant to  $0.001^{\circ}$ , but such constancy is seldom required since the absolute value of the temperature is not often known within  $0.01^{\circ}$ .

As however  $25^{\circ}$  in Europe and  $35^{\circ}$  in tropical countries are temperatures which can be maintained most conveniently it would obviously be advantageous if these temperatures were standardized and all determinations carried out thereat.<sup>1</sup>

**Construction of a Thermostat.** A suitable thermostat for laboratory use comprises a copper tank 60 cm.  $\times$  40 cm.  $\times$  40 cm. which is lagged to reduce the effect of variation in external temperature. A suitable lagging consists of slag wool in a layer about 3 cm. thick. The vessel is placed in a room the temperature of which is fairly constant and which is as free from draughts as possible. At the top of the two larger sides of the tank are plate-glass windows 15 cm.  $\times$  60 cm. to enable readings to be taken of totally immersed objects. The glass is cemented in position, and is held in a metal frame secured to the tank, rubber gaskets being fixed between the metal and the glass. Such joints are water-tight, and the glass is readily replaced when necessary. With gas heating the bottom of the tank is left unlagged, with electrical heating it is protected in the same way as the sides. A constant-level arrangement of the type used on water-baths is necessary at temperatures much above the ordinary. Finally a drain-cock is fitted for emptying purposes. In Fig. 1 (VI), a thermostat with gas control is shown in outline.

**Stirring.** For the thermostat to be efficient, vigorous stirring is essential; three or four paddle stirrers fixed in a frame and driven by an electric motor are suitable. (See next section on Stirrers.) Agitation by compressed air is also an efficient method of stirring the thermostat liquid.

**Gas Regulator.** In order that a given temperature may be maintained constant it is essential that the heating of the bath should be varied suitably

<sup>1</sup> Rae and Reilly, *Chem. News*, 1918, 117, 181.



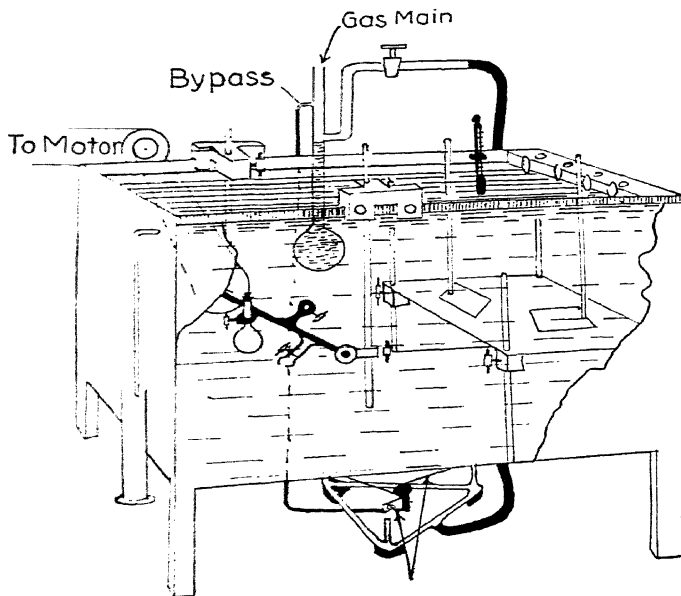


FIG. 1 (VI)

and continuously, so that if the temperature rises the quantity of heat supplied falls, and vice versa. With gas heating this is most successfully accomplished by means of the Lowry thermo-regulator. Various forms of the regulator are shown in Fig. 2 (VI), *a*, *b*, *c*, *d* and *e*. One form consists (Fig. 2 (VI), *d*) of a series of flattened bulbs one above the other; the top bulb is sealed to a narrow tube, one end of which passes to the bottom of the lowest bulb, and the other projects above the water. The object of this particular form is to expose as large a surface as possible, so that the liquid in the regulator will follow the small changes in the temperature of the bath with as small a lag as possible. The narrow tube which projects above the surface is expanded to about 1 cm. in diameter and has a side tube sealed on; the top of the wide tube is closed with a rubber stopper carrying an angle tube drawn out to a fine capillary; the end of the capillary is cut off or ground square, and passes down into the narrow tube. The angle tube and the side tube of the regulator are connected by an H-tube with a glass tap in the middle which acts as a by-pass. The upper tube of the H is connected to the gas supply and the lower tube to a bunsen burner. The latter has the upper tube removed and is lighted directly at the internal pinhole. The by-pass is adjusted so that the gas which passes this way is almost sufficient to maintain the temperature of the bath at the required value; very little gas then passes through the regulator, with the result that the amplitude of the temperature oscillations is small and the mercury is not so readily fouled by sulphur in the gas. Micro bunsen burners are also used. If the gas contains much sulphur it should be passed through

a soda-lime tube. The liquid used in the regulator should have a large coefficient of expansion, a low density and a low specific heat; toluene is very generally used for moderate temperatures. The regulator is filled in the following manner: The toluene is first distilled, and is then repeatedly shaken with mercury to remove sulphur compounds, so that a clean mercury surface left in contact with the toluene will remain clean. The end of the regulator is closed with a stopper carrying a glass tube with a tap in it, and the side tube is connected by way of a tap to the water-pump. The regulator is exhausted and the tap is closed; the regulator is then inverted, the tube placed under toluene, and the tap opened so that some of the toluene enters; the tube is then again exhausted and some more toluene admitted. This operation is repeated several times until the apparatus is

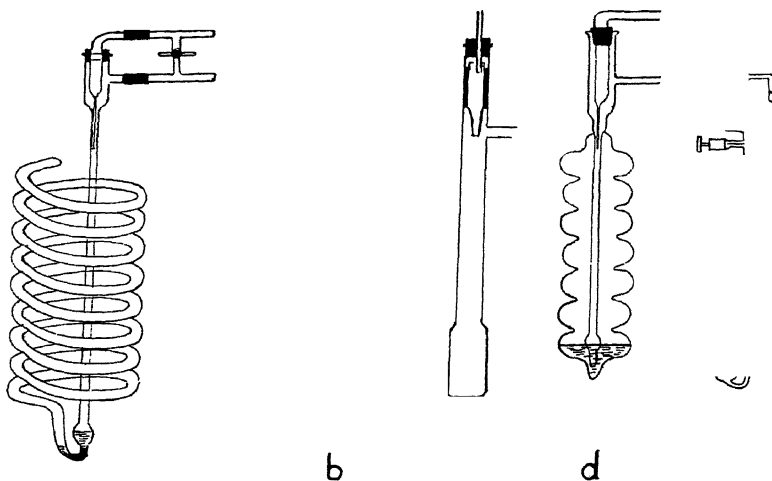


FIG. 2 (VI)

full; mercury is next added so as to nearly half fill the lower bulb, and the excess of toluene is removed. The regulator is placed in the bath at the right temperature, and mercury is added or removed by a capillary tube. The final adjustment is made by replacing the rubber stopper and raising or lowering the capillary tube. A side tube is sometimes added containing a space filled with mercury into which projects a metal screw passing through a threaded hole in a round steel nut cemented on to the end of the tube; by turning the screw the position of the mercury can be adjusted very quickly so as to give the required temperature; the arrangement does not commend itself for very accurate work, and is likely to lead to small chance variations of adjustment which might not be noticed until too late. The mode of action of the regulator will be apparent. If the temperature rises the expansion of the liquid cuts off the gas passing through the regulator. When it falls the contraction of the liquid permits

more gas to pass. For temperatures above  $100^{\circ}$  the liquids in the bath and regulator are chosen accordingly. At such temperatures accurate control is difficult to maintain.

**Electrical Control.** The Lowry thermo-regulator can also be employed in conjunction with electrical heating. The bath, stirring gear, and thermometer remain as before; as heaters two hot-point immersion heaters are used capable of taking 2 or 3 amps. at 100 volts; one of these replaces the by-pass in the gas-heated arrangement, the other is operated by the thermo-regulator. The former is connected to the mains with a choking coil or lamps in series to regulate the current, so that by itself this heater will keep the temperature just below the required value; instead of the heaters, carbon-filament lamps may be used. The thermo-regulator (T.R., Fig. 3 (VI)) has a thick platinum wire sealed into the bottom, making contact with the mercury inside. The other contact is a platinum wire mounted on a thin brass rod on which a screw thread is cut, and with a head having a milled edge at the top; the screw moves through a nut cemented into the top

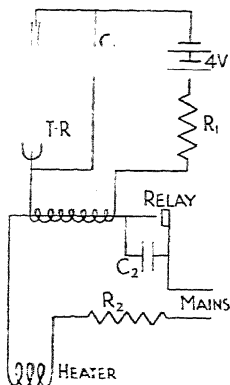


FIG. 3 (VI)

of the regulator and provides an easy method of adjustment. The side tube of the regulator is closed with cotton-wool. The regulator is in series with two storage cells, a 2,000 ohm sliding rheostat,  $R_1$  and a Post Office standard relay; a current of a few milliamperes is sufficient to work the relay, but to prevent sparking with consequent injury to the contacts a condenser  $C_1$  of 0.5 microfarads is connected in parallel with the terminals; the condenser may be replaced by a pair of aluminium plates insulated by glass tubing and held together by two rubber bands; the plates are about 8 cm. by 10 cm., and are immersed in a beaker of distilled water. The second heater is connected in series with the mains, a lamp resistance,  $R_2$ , and the relay, the contacts being again shunted with a condenser  $C_2$ . When the temperature rises contact is made in the regulator; the current from the storage cells then operates the relay, breaking the contact in the heating circuit. When the temperature falls, the current in the relay ceases; the spring in the relay then pulls the arm back, and again makes the heating current. Either of these thermostats will keep the temperature steady within  $0.01^{\circ}$  for weeks.

Fig. 4 (VI) shows a form of thermo-regulator for electrical heating<sup>1</sup> which operates without the use of a relay. The tube A contains toluene and B mercury. The mercury level can be adjusted by means of the screw C. The upper part of the apparatus at D is filled with condenser oil. Filling is carried out at D, which is then closed with a rubber stopper. Platinum wires are sealed in at E and Pt. The regulator is connected in series with the heater and is operated with 8 volts obtained from a small 50-watt transformer connected to the mains: a condenser of 1 microfarad is connected in parallel with the electrodes to prevent sparking. When the bath becomes too hot the expansion of the toluene breaks the circuit at E and

<sup>1</sup> Centnerszwer and Szper, *Bull. Soc. Chim.*, 1937, 495.

the heater is thrown out of operation. As the temperature falls and the toluene contracts the mercury rises at E and makes the current. An auxiliary heater working continuously by itself maintains the bath at a temperature slightly below the working temperature.

### Bimetallic Helix Temperature Control.

Klopsteg and Stannard<sup>1</sup> describe a device designed to control a 5-litre oil bath at 100° within limits of 0.05°. The helix consisted of strips of brass and invar welded together. With this type of regulator operating an electrical heater, the pressure between the contacts when at the desired temperature is zero, but the contacts are liable to stick, and before separation occurs there must be a further drop in temperature in order to separate them: as the temperature rises and reaches the desired temperature, the pressure between the contacts is very small, so that the resistance is high and a further rise of temperature must occur before the contacts are well pressed together. Furthermore, dirt between the contacts may cause trouble. To obviate the last, one of the contacts is a rotating silver cylinder and the contact is made on the cylindrical surface.

The bimetallic helix is placed vertically in the oil-bath with its upper end fixed: the lower end is attached to a vertical rod which passes up the axis of the helix and of course as the helix heats or cools this rod rotates in one direction or the other. On the top of the rod is keyed a toothed wheel engaging with a screw, and by turning this the temperature may be adjusted to the required value. A horizontal lever attached to the top of the rod carries the contact which engages with the rotating cylinder contact. Behind the contact on the lever is a soft-iron armature and inside the silver cylinder is an electromagnet in series with the heater and the contacts. When contact is made, the electromagnet is activated, and attracts the armature so that a definite pressure is established at once at the contacts.

There is also in series with the heater an interrupter consisting of a rotating metal cylinder with an insulating segment. When contact is made the current starts and persists until the interrupter breaks the circuit: if the heat input has been sufficient and the lag sufficiently short, the lever contact will move away from the cylinder and contact will remain broken, only to be remade when the regulator has responded sufficiently to the cooling of the bath: if the heat input is not yet sufficient contact will be remade as soon as the insulating segment has passed. By this means the current is always broken at the interrupter and never at the control contacts so that there is no sparking here: sparking on the interrupter is reduced by a condenser. The pressure between the control contacts makes it possible to use a high rate of energy input.

**Thyratron Relay for Thermostat.** Fig. 5 (VI)<sup>2</sup> shows a circuit using

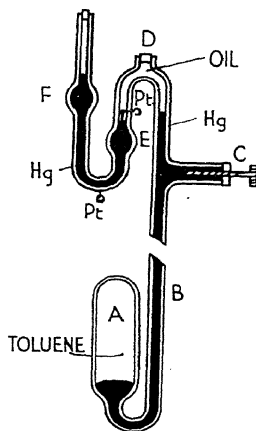


FIG. 4 (VI)

<sup>1</sup> *J. Opt. Soc. Amer.*, 1923, vol. 7.

<sup>2</sup> The diagram is from D. Belcher, Thesis, Cambridge, 1937.

a gaseous (Thyratron) valve. One great advantage of this form of relay is the elimination of sparking at the mercury surface in the regulator, so that this surface is no longer fouled by oxidation.

The gas-filled valve differs in three important respects from the vacuum valve. In the first place, as the voltage of the grid G is made less and less negative with respect to the cathode F of the valve, nothing will happen until a certain critical voltage is reached, and then the full anode current flows at once, limited only by the cathode emission and the external load resistance, i.e. if the tube passes 1 amp. when conducting it will pass 1 amp.

no matter what the grid voltage is, so long as it is sufficiently positive. The second characteristic of the tube is the large quantity of electricity it will pass, i.e. amperes instead of milliamperes. Thirdly, once the grid has reached the necessary potential to start the current it loses control completely and the only way the current can be stopped is by the removal of the plate positive voltage.

In the circuit shown, F is a fuse, S a switch, and M the heater for the bath. Z is a transformer to reduce the 200 volts A.C. to 2 volts for the heating of the

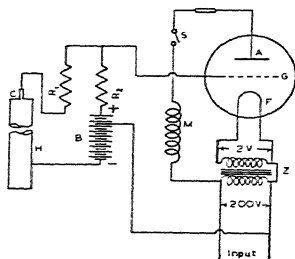


FIG. 5 (VI)

filament F. H is the thermo-regulator.

With contact in the regulator at C, when the bath is too hot, the battery B maintains the grid G at a negative potential with respect to the filament, so that no current flows through the valve: the current flowing from the battery through the contact C is limited by the high resistances  $R_1$  and  $R_2$ . As the bath cools, contact is broken at C; the battery B now makes the grid positive with respect to F, the full current then flows through the valve and the heater M. Since A.C. is being used at the input, the plate A becomes negative in each cycle and the current stops, but it will restart in the next half cycle when A becomes positive, provided that the contact at C is still broken and the grid is still positive. When the bath heats up contact is made at C and the grid becomes negative, so that in the next half cycle when A becomes negative the current in the valve stops and does not restart until the regulator again cools. This form of regulator is found to be very effective. (See Conductivity, Chapter XI\*, Section 2, for fuller description.)

**Thermostats for Low Temperatures.** For some purposes it is necessary to use a thermostat adjusted to some temperature between zero and the room temperature; the heating arrangements of the ordinary thermostat can then be replaced by a coil of thin-walled copper tubing carried round the walls of the thermostat near the top; ice water is passed through the coil, and the temperature is controlled by a thermo-regulator working a relay which cuts off the supply of ice water by pinching a thin-walled rubber tube. The top of the thermostat may be covered with plate glass cut in three strips for convenience in removing. Greater accuracy than  $0.01^\circ$  cannot be obtained at these temperatures.

Alternatively, water below the temperature it is required to maintain

is run into the bottom of the thermostat through a coil which is heated by a burner controlled by the regulator. The head of water flowing into the coil is kept constant so that a constant current of water is obtained. The water is led away from the thermostat at the top. With a good flow of water no stirring is needed.

Morgan devised an arrangement for maintaining a small thermostat at any desired temperature between  $0.1^{\circ}$  and  $90^{\circ}$  to a few hundredths of a degree. The regulator has a U-shape, one arm of the U being 3 cm. in diameter and 15 cm. long, and closed by a tap with a funnel above it. A platinum wire is sealed in this side, and bends vertically down so as to reach a point about 1 cm. above that at which the tube narrows. The bend of the U-tube is a capillary of 0.75 mm. diameter. About 6 cm. above the bend this expands to a diameter of 4 mm., which continues to the top of the tube; to the end of the tube is fixed by means of a thumb-screw a threaded collar with a binding screw. A threaded brass rod 2 mm. in diameter passes through the collar and terminates in a short stout platinum wire. Mercury is added to within 3 cm. of the top of the capillary; and then purified toluene is poured in to fill the larger side tube. The stopcock is left open while the temperature of the bath is roughly adjusted to the required value, and is then closed, the final adjustment being made by means of the threaded brass rod. The two wires from the regulator are connected to a 2-volt cell and a relay which will operate so as either to make or break the current in the main circuit. The connection in a P.O. standard relay can be made so as to produce either result. The main circuit may consist of D.C. current from the mains passing through a 32 watt lamp, and an electro-magnet arranged like the telegraph sounder, except that the brass bar is prolonged and has a weight of several kilograms attached to it, so that when no current passes the weight causes the other end of the bar to press upwards against a metal stop. Between the latter and the bar passes a thin-walled rubber tube which is compressed so that no water can flow through it. The bath has an overflow so as to keep the water-level constant, and ice water or hot water from a reservoir giving a pressure head of 40 to 50 cm. passes into the bath through the rubber tube. At temperatures below that of the room the electric circuit is arranged so as to cut off the current and allow ice water to flow when the expansion in the regulator makes the current there. For higher temperatures the connections are arranged so as to break the main current, and cut off the hot-water supply when the temperature causes the regulator to make the current in the relay. Thermostats to give exactly  $0^{\circ}$  are rather difficult to arrange. Since water just above  $0^{\circ}$  is less dense than that at  $0^{\circ}$  it is advisable to have a good supply of ice at the bottom of the tank. A false bottom of perforated zinc is therefore fitted 15 to 20 cm. above the bottom of the bath, and on this rests a rectangular perforated zinc box of such a size as to leave ample space for ice between it and the sides of the bath; the box forms the actual working space, and can be fitted with a stirrer, &c. When preparing the thermostat for use crushed and washed ice is packed on the bottom to a height of 15 to 20 cm.; the false bottom is then secured in position, and on this the rectangular box; the space between the walls and the box is then packed with lumps of ice up to the top; ice

water is next run in to the desired level, and finely crushed ice is put in to a depth of 2 or 3 cm. in the top of the box and a plate-glass cover placed on the whole.

Woog, Givaudon and Dayan<sup>1</sup> describe an apparatus which is readily constructed and which can be regulated by hand to maintain a temperature of  $-60^{\circ}$  to  $0.1^{\circ}$ . Such a cryostat is useful for example in studying the viscosity of lubricants at low temperatures.

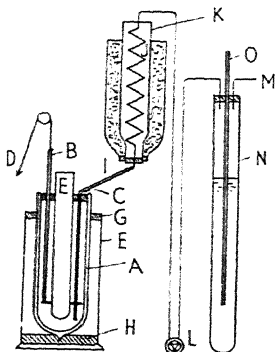


FIG. 6 (VI)

In Fig. 6 (VI) A is a 750-ml. Dewar flask containing cooled acetone which is mechanically stirred by B at the rate of once per second. The rod of B is of glass to prevent the deposition of hoar frost which would occur on a metal rod. An alcohol thermometer is used to obtain the temperature of the acetone. The experimental tube E is fixed by a cork in the centre of the flask A, which is itself supported with cork at G and H in the glass jar F. The inside of F and the outside of A are coated with a mixture of glycerine and alcohol to keep them transparent. The glass tube I, which is well lagged in its course through the air, is connected to the thin copper worm J and this to the three-way tap L and the Mariotte bottle N. M is a connection to a pump. J contains acetone and

carbon dioxide snow and as shown is well lagged with glass wool. By raising or lowering the open tube O the vacuum in N can be maintained at any desired degree, so that on opening tap L to connect to J acetone may be drawn up from A to any height in J.

At the start the acetone in A is cooled by the addition of carbon dioxide snow. The alcohol thermometer is watched, and as the temperature rises the tap L is turned so that a little acetone is drawn up into the cooler J: the height to which it is raised and the time it should stop in J are soon found by experience. The tap L is turned to connect I to the atmosphere and the cooled acetone falls back into A. The temperature in A fluctuates about  $0.3^{\circ}$  about the mean value, but that in the inner vessel varies less than  $0.1^{\circ}$ .

**For high temperature** an electric furnace is described by Waidner and Burgess. It consists of a resistance furnace mounted vertically, having two separate heating coils of platinum ribbon 0.01 mm. by 2 cm. wound on porcelain tubes with the turns so spaced as to allow the establishment of a uniform temperature over a considerable length of the furnace. A separate rheostat controls the current in each circuit. Temperatures are read by means of a platinum resistance thermometer, and it is possible, by adjusting the rheostats by hand, to maintain the temperature steady to a few hundredths of a degree.

For another account of thermostats and for a review of some recent improvements the article on 'Thermostats' by Swallow<sup>2</sup> may be consulted.

<sup>1</sup> *Bull. Soc. Chim.*, 1933, 240.

<sup>2</sup> *Thorpe's Dictionary of Applied Chemistry*, Supplement, 1935, Vol. II. Longmans, Green & Co., London.

## SECTION 2: STIRRERS

In the last section, reference was made to the need for efficient mixing in keeping the temperature constant. In this section, the general problem of agitation of liquids will be considered.

A simple and effective stirring can be obtained by blowing air through the liquid and some modern laboratories have air-compression installations. Small apparatus can be had with as low as 150 cubic feet per hour displacements which are not expensive to run. Among mechanical stirrers a common arrangement is that in which two straight glass rods are held by screws in sockets in a horizontal arm fixed to the pulley and capable of rotation. The straight rods may be replaced by bent rod. Such a form of stirrer does not give much vertical mixing, however, and where this is desirable the simple agitator is best replaced by some form of screw

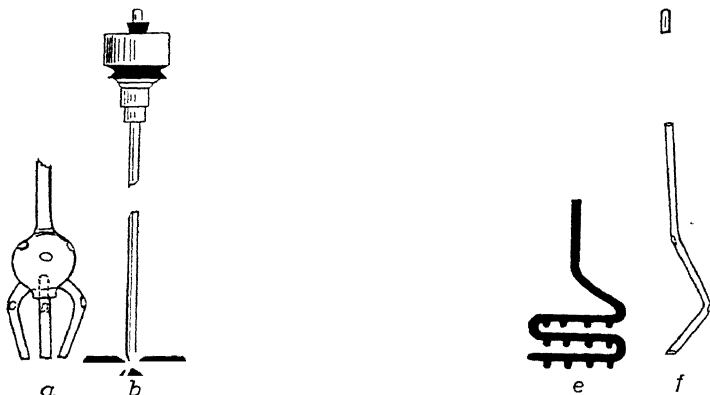


FIG. 7 (VI)

or bladed stirrer. See Fig. 7 (VI) (*a*, *b*, *c*, *d*, *e* and *f*). Form *e* is improved if the three bottom rods are sloped about  $45^\circ$  to the horizontal.

A stirring apparatus devised by Dupré (Fig. 8 (VI)) consists of two glass stirrers with vanes, rotating in opposite directions. This motion produces thorough stirring and prevents the circular rotation produced with the ordinary stirrer.

**Mode of Entry of Stirrer.** In the simplest form the bearing consists of a piece of glass tubing through which the stem of the stirrer passes, fitting closely but without much friction. The glass and tubing pass through a rubber cork which is held vertically in a clamp or other support. The projecting upper end of the stirrer is attached to a pulley which can rest on the edge of the glass tube (Fig. 9 (VI)).



Instead of glass tubing, metal bearings can also be used, and the pulley may be fitted to the stirrer by means of a rubber stopper. A useful form of permanent bearing is shown in Fig. 10 (VI). Any desired form of stirrer may be attached by passing it through an adjustable conical collar which can be screwed down to hold it by means of a nut.

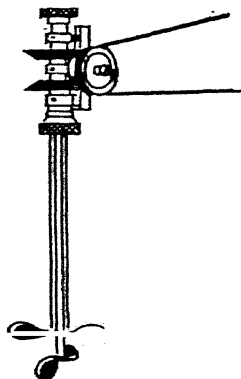


FIG. 8 (VI)

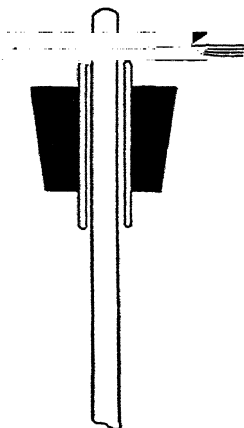


FIG. 9 (VI)

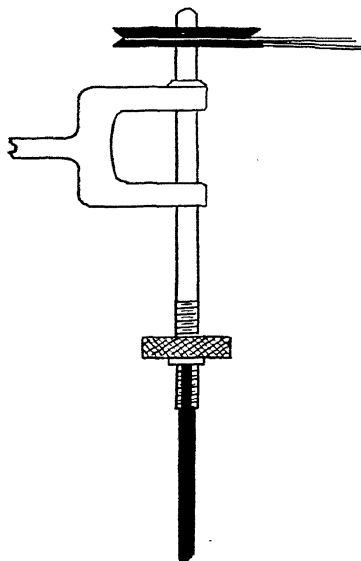


FIG. 10 (VI)

**Gas-tight Stirrers.** These must be used when gaseous products of a reaction have to be collected or access of air prevented. Fig. 11 (VI), *a*, shows the construction. To the axis of the stirrer is fixed a wide piece of tube, and to the bearing a still wider piece. The space between the wider piece and the bearing contains mercury (or water if it is otherwise suitable). Instead of sealing on the pieces of tubing they can be kept in position by corks as in Fig. 11 (VI), *b*. A simple form of mercury seal of this type is shown in Fig. 11 (VI) *c*. For further details, see Chapter XIII, Section 5 on Rates of Reaction, where the working of this apparatus is described.

The mercury seal has been replaced in recent years to some extent by soft-metal surface joints. In this group is included the metal-clad joint of the Scientific Glass Apparatus Co.<sup>1</sup> These joints do not lock and are not affected by corrosion. The soft metal surfaces mend together and form a perfect seal. They also uncouple quite readily after use. No metal is exposed to corrosive action of vapours and this apparatus is easily adapted to use in a distillation unit. The stirrer, bearing, and shaft fit precisely to one another. Inner surface dimensions of the bearing tube are accurate within

<sup>1</sup> New Jersey, U.S.A. Pat. No. 2,083,228.

$\pm$  1 to 2 microns. Even at 1,000 r.p.m. the minimum life of the bearings is 1,000 hours. No supplementary seal or stuffing-box is needed, and difference of pressure as great as 100 mm. of mercury between the inside and outside of the flask causes no leakage.<sup>1</sup>

Interchangeable ground glass joints eliminate the use of cork and rubber stoppers, and join unit parts of a complete apparatus into one rugged piece. In order to stir solutions in a flask equipped with these joints, and be able to do so under vacuum, it became necessary to develop a stirrer which could be controlled from outside of the flask<sup>2</sup> and yet be sealed to hold a vacuum

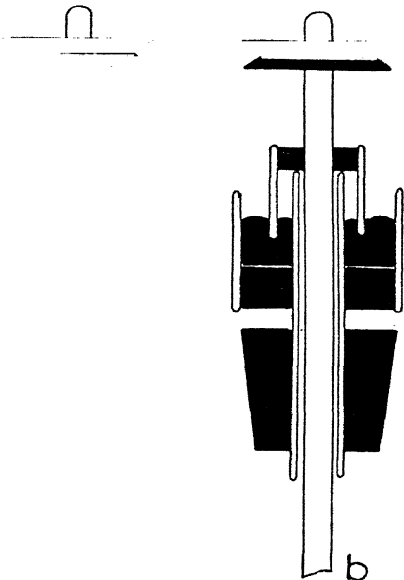


FIG. 11 (VI)

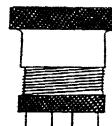


FIG. 12 (VI)

inside of the flask, Fig. 12 (VI). This unit is the latest of packed vacuum stirrers.

The interchangeable ground glass joint is used in order that the same stirrer may be attached to any size flask having a 29/42 joint. In Fig. 13 (VI)<sup>3</sup> the stirring apparatus is shown in a complete apparatus.

In place of the gas-tight stirrers mentioned in the previous paragraph, another device can be applied in some cases with greater advantage. This consists in the use of a stirrer which is contained in an enclosed space (to exclude moisture, &c.) and activated by means of an electromagnet.<sup>4</sup> In

<sup>1</sup> Supplied by Fish-Schurman Corporation, New York.

<sup>2</sup> Made by Scientific Glass Apparatus Co., New Jersey. Cat. No. J1169A.

<sup>3</sup> *Ibid.*, Cat. No. J1169.

<sup>4</sup> Reilly and Donovan, *Sci. Proc. Roy. Dubl. Soc.*, 1930, 19, 33, 412.

the determination of molecular weights of hygroscopic substances by alteration in the melting point such an apparatus is practically essential (see section on molecular weight determination). The liquid is stirred in a closed

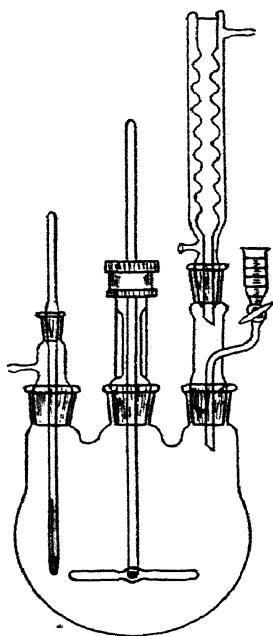


FIG. 13 (VI)

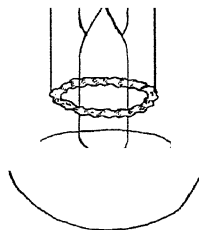
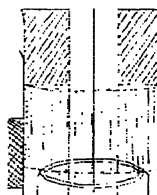
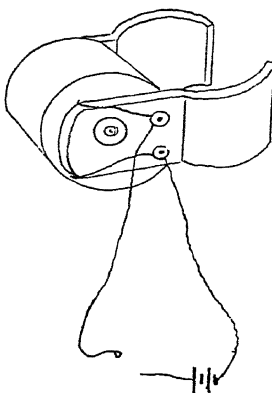


FIG. 14 (VI)

tube by a platinum or nickel stirrer, with an iron top, which is lifted by an electromagnet round the top of the tube, which is connected to a 'make and-break' attached to two secondary cells. In Fig. 14 (VI) the front view of the solenoid round the tube containing the thermometer, solution, and

stirrer is shown, and the side view shows the solenoid attached to the 'make and break' and cells.

If high voltage direct current (e.g. 230 volts) is supplied to the laboratory it may be utilized indirectly instead of employing a number of secondary cells. In this connection the following modified apparatus has been devised.<sup>1</sup> The original electromagnet was constructed to work from a 4- or 6-volt accumulator. It was unwound and altered as follows (see Fig. 15 (VI)) : (a) The bobbin B was stripped and rewound with as many turns of No. 38 s.s.c. copper wire as it would hold. (b) Platinum points were inserted at C<sub>1</sub> and C<sub>2</sub> shunted by a condenser D to decrease sparking. (c) A small leaf spring was fitted with its tongue acting on contact C<sub>2</sub> to effect a quick break, as formerly the breaking was sluggish in its action. (d) A 230-volt 20-watt lamp was put in series with electromagnet. (Note.—For 110-volt supply insert a 40-watt or 60-watt 110-volt lamp.) With the modified apparatus very little sparking occurs, and it can be worked for long periods without attention.

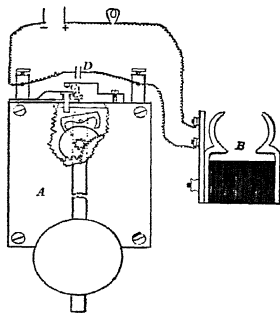


FIG. 15 (VI)

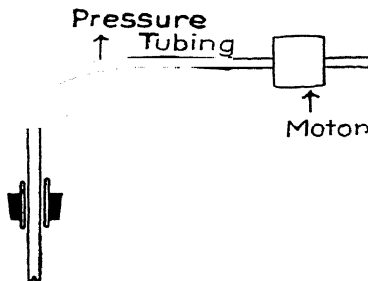


FIG. 16 (VI)

**Motors for Stirrers.** As a source of power for stirrers water turbines and hot-air motors are sometimes used, but are now usually replaced by small electric motors. Transmission can be carried out by systems of pulleys or direct coupling may be used. A convenient form of direct coupling is obtained by connecting the axis of the motor to the stirring rod by pressure tubing (Fig. 16 (VI)).

**Up-and-down Motion.** For stirring liquids in narrow columns, e.g. in the estimation of the lowering of freezing-points in the Beckmann apparatus, the stirrer consists of a ring attached to a vertical rod which is given an up-and-down motion. An eccentric, which may be made from two pulleys, is used to obtain this form of motion from the ordinary rotary motion provided. Fig. 17 (VI) explains the mode of action. (If the points of attachment A and B are varied, the extent of vertical movement can be varied within wide limits.) Pulleys can be obtained in which the points of attachment, A and B, slide in radial grooves, and can be fixed easily at any desired distance from the centres of the pulleys.

**Shaking Motion.** The two common forms are the 'end-over' shaker

<sup>1</sup> Reilly and McKenna, *J. Sci. Inst.*, 1931, 8, 4, 134.

and the 'to-and-fro' shaker. In both provision is made for use by hand, or mechanically. By altering the position of the connecting-rod on the driving wheel in the 'to-and-fro' shaker the extent of the excursion of the truck can be varied. A form of this shaker in which an angled connecting rod is used, and in which the driving wheel is not attached to the board which carries the truck, can be used in water-baths, where it is required to shake at a constant temperature, as the truck and stand can be submerged, and the driving wheel mounted above the bath.

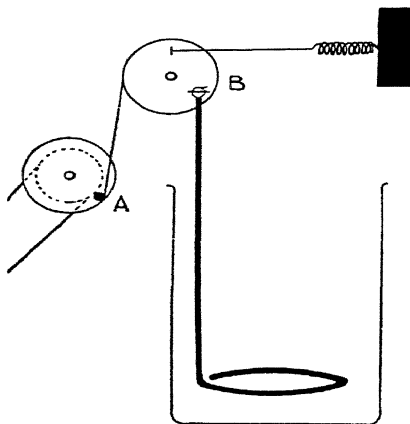


FIG. 17 (VI)

### SECTION 3: DRYING AND EVAPORATING APPARATUS

**Desiccators.** For most practical purposes the ordinary glass desiccator with sulphuric acid, calcium chloride, soda lime or phosphorus pentoxide as drying agent may be employed. Sodium hydroxide has also some advantages in special cases as a desiccating agent. For greater efficiency it is better to have the apparatus supplied with opening and tap so that it can be evacuated. For higher temperatures desiccators made of thin glass have been constructed which can be placed in a water bath or air bath. Where it is necessary to concentrate solutions at low temperature<sup>1</sup> this can be done in a vacuum desiccator of the type of a bell jar placed on a glass plate with two flat surfaces, slightly greased. In the ordinary course evaporation may take a long time owing to excess of cooling due to latent heat losses. If necessary a small carbon electric bulb may also be placed in the bell jar and this is lit from time to time to supply heat when the temperature falls. For the drying of small amounts of substance at definite temperatures the apparatus shown in sketch is convenient and very efficient. The substance is contained in an inner tube which is surrounded by a vapour at a definite temperature. The bulb A contains phosphorus pentoxide and the tap leads to a vacuum apparatus (Fig. 18 (VI)).

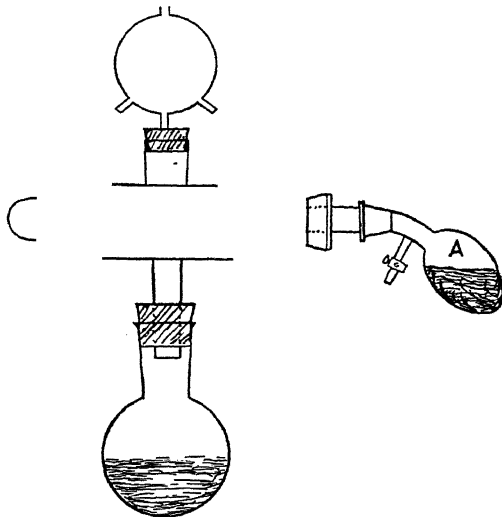


FIG. 18 (VI)

The substance is contained in an inner tube which is surrounded by a vapour at a definite temperature. The bulb A contains phosphorus pentoxide and the tap leads to a vacuum apparatus (Fig. 18 (VI)).

**Intensive Drying.** For exhaustive drying, two types of apparatus are used, in which a glass spring pressure-gauge or a mercury indicator is employed. They are made of glass which is free from capillaries in the walls of the tubing. These latter if present might retain moisture. Fig. 19 (VI) shows an apparatus devised by Smits for the long storage and drying of substances. Phosphorus pentoxide is distilled into vessel B through *b* in a current of dry oxygen. Special precautions are taken while introducing the substance to S to prevent moisture entering. S is then cooled in liquid air and *s* and *b* sealed off. The connection *c* is joined to a high vacuum

<sup>1</sup> Morgan and Reilly, *Trans. Chem. Soc.*, 1913, 103, 812.

pump and then the tube closed. The dry substance in S is next distilled into the phosphorus pentoxide and the apparatus sealed off until required for subsequent examination. In a second type (Fig. 20 (VI)) Smits constructs an apparatus of capillary free glass which is filled as follows. In bulb A is placed distilled phosphorus pentoxide and tube D sealed off while a strong current of dried nitrogen is passing in the opposite direction. Bulb B is then filled in the same way with the substance to be studied, and after cooling the bulb, tube E is sealed off as short as possible. Subsequently

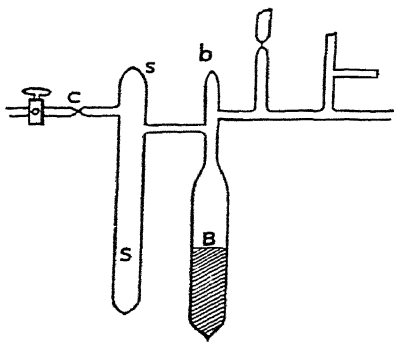


FIG. 19 (VI)

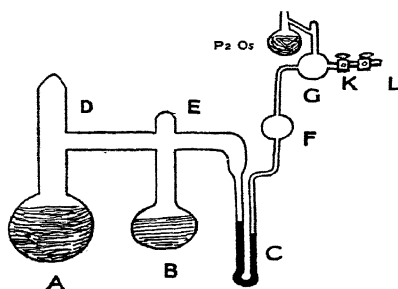


FIG. 20 (VI)

bulb G is filled with about 10 ml. of pure dried mercury and sealed. Tube L is connected to a high vacuum pump, whilst B is cooled in liquid air and bulb A is heated in a water bath at  $80^{\circ}$ . In the meanwhile, the mercury is heated to drive out dissolved air. After closing cock K, the substance in bulb B is heated and then cooled again. Cock K is then opened and the apparatus re-evacuated. K is closed and the connection to the high vacuum broken. The tubes C are filled with mercury by inclining the apparatus. This apparatus can be modified so that a repeated circulation of the vapour through a series of phosphorus pentoxide bulbs can be arranged.

**Ovens.** Substances which do not decompose at  $100^{\circ}$  are usually dried in a *water-oven*. This is commonly a more or less cubical copper vessel which is surrounded by a jacket containing boiling water the level of which is kept constant by means of an overflow and a water feed. In some ovens a constant water level is secured without any feeding system by attaching a ball condenser to the top. If this is efficient there is no need to refill the jacket once it has been filled to the proper level. In a third type these features are combined together with slight alterations so that the condensed steam from the jacket, instead of flowing back again, is led away and provides distilled water, the level of the water in the jacket being maintained by a feed and overflow arrangement. This is a very convenient form of oven for smaller laboratories where steam is not laid on, and distilled water is scarce. The use of ovens for the preparation of distilled water is not considered advisable, as trouble often occurs with deposits in the oven from the evaporated water. If the oven is fitted with a detachable base this difficulty

is lessened as it can be removed for cleaning. Such an oven is described by Sand.<sup>1</sup>

If the substance does not easily decompose drying may be facilitated greatly by working a few degrees above 100°. For this purpose toluene, boiling approximately at 110°, may replace water in the jacket, or crude xylene, boiling at 129°, if a somewhat higher temperature is required. Still higher temperatures can be obtained by the use of oil or glycerine in the jackets. In this connection and also in the jacket in vapour density determinations, special liquids are required. The attached table gives a list of suitable liquids. In some water ovens the entering air is preheated by passing first through a flat coil in the oven jacket. This device is useful where it is desired to keep the temperature at 100° as exactly as possible. The following table gives a list of substances suitable for maintaining a constant temperature vapour bath. They may also act as a jacket in vapour density determinations at high temperatures.

SUBSTANCES FOR CONSTANT-TEMPERATURE

Liquid	B.P.	Liquid	B.P.
Methyl formate . . . .	32°	Ethyl toluene . . . .	160°
Ether . . . . .	35°	Aniline . . . . .	184°
Acetone . . . . .	56°	<i>o</i> -Toluidine . . . . .	200°
Chloroform . . . . .	61°	Nitrobenzene . . . . .	209°
Methyl alcohol . . . .	65°	Naphthalene . . . . .	218°
Ethyl alcohol . . . . .	78°	Quinoline . . . . .	238°
Benzene . . . . .	80°	<i>α</i> -Bromonaphthalene . .	280°
<i>n</i> -Propyl alcohol . . . .	97°	Diphenylamine (m.p. 54°)	310°
Water . . . . .	100°	Triphenylmethane . . . .	353°
Toluene . . . . .	110°	Anthraquinone . . . . .	380°
<i>n</i> -Butyl alcohol . . . .	117°	Sulphur . . . . .	445°
<i>m</i> -Xylene . . . . .	139°	Phosphorus pentasulphide	518°
Phenyl bromide . . . .	156°	Stannous chloride . . . .	606°

The above boiling-points are at normal pressure.

For higher temperatures than these quoted an electric furnace may be employed. For temperatures up to 1,600–1,700° porcelain may be employed as a container for the vapour, but for higher temperatures a platinum container is necessary. For temperatures above 2,000° an iridium container is necessary and this is lined on both sides with fused magnesia and magnesium chloride so as to render it impervious to gases and vapours.

**Air-ovens** are usually employed, however, for high-temperature work, and have the advantage of heating up rapidly, though the temperature is not so easily kept constant and is likely to vary considerably from point to point. They are usually made of hard copper or sheet iron and are directly heated by a bunsen or ring burner or by rose burners. The substances to be dried or heated should be placed on the perforated shelf and not on the bottom of the oven, as the temperature is there much too variable. Ovens are usually fitted with an adjustable opening in the lower part of the door

<sup>1</sup> *J. Chem. Soc.*, 1929, 214.



for the admission of air, and have another opening at the top to let the hot air escape. The current so set up facilitates drying. Ovens are provided with an aperture at the top to hold a thermometer. The thermometer bulb should be as close as possible to the object which is being heated.

Hearsons make an air oven with a metal tube thermostat which can be set for temperatures from 50° to 250°. The Freas Oven (A. H. Thomas) can be obtained with ranges from 70° to 180° or 260°. The 12 in. × 12 in. × 12 in. size takes 600 watts.

The Bara electric oven<sup>1</sup> is an example of an oven well suited for a physical chemical laboratory. It has a range of 20° to 200° with a constancy  $\pm 1^\circ$ . The actual heating space is 10 inches high, 9 inches wide and 8 inches deep. The thermostat is of the bimetallic type. It has a dial setting on a scale numbered from 20° to 200°. The controls are found behind a separate door fitted with a lock and key, so that there is no chance of anyone save the operator altering the regulator. The thermometer, which is flush with the outside of the door, protrudes about 2 inches into the interior of the oven and is protected by a guard on the inside.

The outer casing is made of hard asbestos compound, and the handle and hinges are chromium plated. The oven is therefore easily kept clean and free from dust and dirt.

The inner chamber is lined with stainless steel, providing a resistant surface readily cleaned; the shelf is perforated to allow free circulation of air, a necessary condition to equalize temperature.

Two pilot lamps are fitted; one, which shows a red light, to indicate that the oven is switched on, and a second which shows a green light to indicate the making and breaking of the heating circuit by the thermostat.

The maximum consumption, with all sections of the heating circuit in use, is 800 watts; the average consumption at 150° being 300 watts.

For electric furnaces up to a normal maximum operating temperature of 1,000° or for high temperature furnaces designed for working range of 1,100–1,400°, the special furnaces made by The Wild-Barfield Electric Furnaces, Ltd.,<sup>2</sup> can be recommended from experience. These furnaces can be obtained in a variety of sizes, from the smaller types suitable for laboratories to the very large sizes required for technical operations. Some special features of these furnaces may be outlined. The refractory chambers on which the heating elements are wound are moulded in a carefully selected clay mixture possessing an exceptionally low coefficient of thermal expansion and highly resistant to thermal shock. The heating resistances are made of pyromic induction melted 80/20 nickel chromium alloy (m.p. 1,390°) and it is free from any tendency to radial cracking or hot-spots. For temperatures up to 1,400° special recrystallized carborundum 'elements' are used. A safety device can be fitted to protect the windings from accidental overheating. Only one of these ovens will be described here, namely, the rectangular type, which is designed for general laboratory work and heat-treatment of small components, tools and similar work. The smallest size has the following internal dimensions: 203 mm. × 76 mm. × 76 mm., with a maximum input of 0.85 kilowatts; and the largest size has the dimensions: 457 mm. × 229 mm. × 229 mm., with a maximum input of 5 kilowatts. The specification for

<sup>1</sup> Made by Baird & Tatlock, London.

<sup>2</sup> Holloway, London.

the oven is as follows: Substantial sheet-metal case with angle bracing, the upright members being extended to form legs. Front plate of special insulating material reduces end heat losses. Flap-door of plate, with insulating plug pad securely fixed, the whole door carried on malleable iron castings, and arranged to form fore plate when open. Counterbalanced doors embody cast-iron frames, filled with high quality insulating brick, and carried on angle door guides, bearing pulleys, with counterweight and chain. Chamber of highest grade moulded refractory securely supported in case, and wound with highest quality 80/20 nickel-chromium wire, the lead-outs being brought to terminals on porcelain blocks and fitted with strong terminal covers. Highest quality insulation surrounds chamber, reducing heat losses to a minimum. Provision for thermo-couple at back of furnace. Made for 100/250 volts, and suitable for temperatures up to 1,000°, or 960° with standard excess temperature cutout.

A convenient type of small-scale drying cabinet for material on trays is

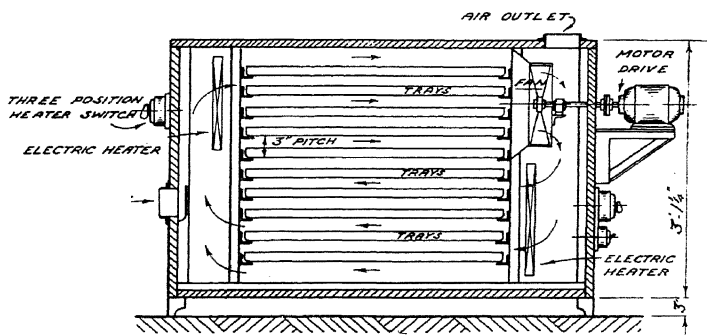


FIG. 21 (VI)

made by L. A. Mitchell.<sup>1</sup> These units may be arranged for heating by steam, gas or electricity. Fig. 21 (VI) shows a sectional front elevation of one of these ovens with an electric element. They comprise essentially a central drying-chamber with rack slides for the trays and end compartments housing the heaters and fan. This fan may be arranged for driving by belt or direct-coupled electric motor, and when running induces a current of air above the trays in the upper half of the drying compartment. The air displaced by the fan then passes through a heating unit and thence into the lower half of the drying compartment, returning to the upper half by way of the heater compartment at the opposite end. During the drying of the material in the stove the moisture is absorbed by the hot air passing across the trays, and to prevent this air from reaching saturation-point (in which state no further drying would be possible) an air outlet and inlet is provided. The amount of air exhausted from the stove may be adjusted by means of dampers, and it should be noted that the relative humidity should generally not be allowed to exceed 70 per cent.

In certain cases, however, notably when drying materials which form a

<sup>1</sup> Peter Street, Manchester.

surface skin on drying, it is advisable to commence the drying operation with an exceptionally high relative humidity, thus preventing surface drying and allowing the centre of the product to dry uniformly.

The temperature of the stove may be adjusted by throttling with gas or steam heating, or by switching off different heating elements with electric heating. Where accurate control of temperature is required, for example when drying material which has a comparatively low melting-point, thermostatic control of the heater units is advisable.

**Film Drum Dryer.** One typical dryer of this type is described. It is the Mitchell drier with patent roller feed.<sup>1</sup> This unit comprises a main drying cylinder carried in heavy pattern bearings on rigid side frames, a lower and an upper, or 'carrier', feed roller, an adjustable feed trough, and a group of scraper or discharge knives securely mounted above a sloping discharge chute. The main drum may vary in size but is usually 5 feet long by 2 feet 6 inches diameter, the outer surface being turned, ground and polished under working temperature conditions. The standard construction is of close-ground cast iron suitable for operating under steam pressure of 30 lbs. per square inch, but the drum, and also the feed rollers, feed trough, and discharge chute, may be made in a variety of special corrosion-resisting

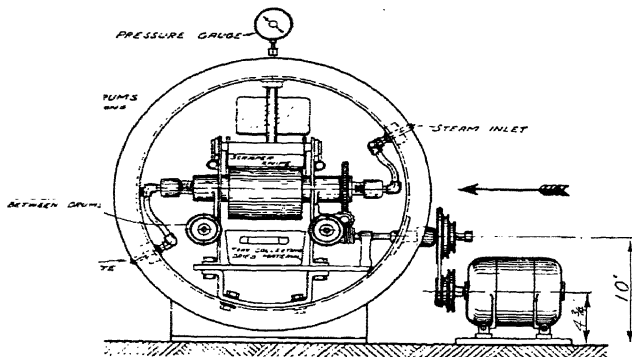


FIG. 22 (VI)

metals to suit individual requirements. Fig. 22 (VI) shows a front elevation view of dryer with door removed.

The working of the machine is briefly as follows: The solution to be dried is fed into the feed trough, which may or may not be jacketed for heating or cooling. Running in the trough is the lower feed roller which is positively driven from the drum drive. A film of solution adheres to the surface of this roller, the thickness of the film being variable by raising or lowering the trough thus varying the depth of immersion of the roller. Immediately above this roller is the top or 'carrier' roller which runs in adjustable bearings by means of which the clearance between the rollers, and thus the thickness of film taken forward by the top roller, may be varied. The top roller, the surface of which runs in the same direction as the surface of the

<sup>1</sup> Made by L. A. Mitchell, Peter Street, Manchester.

drum at the point of contact, then passes the film on to the main drying drum. A final adjustment of the thickness of film applied to the drum is permitted by the mounting of the adjustable bearings for the top feed roller on adjustable swing cradles which can be conveniently adjusted from a handwheel.

As the drum revolves the film of liquor or paste applied by the feed rollers is dried by the heated surface, and in this form eventually comes into contact with a group of scraper knives held firmly against the drum surface. These knives remove the film from the drum in the form of flakes or powder, the flakes falling down a discharge chute into a conveyer or other device for their disposal, whilst the cleared surface of the drum passes round to the top feed roller to repeat the cycle.

The machine may be arranged for driving by belt with fast and loose pulleys, or alternatively by direct-coupled motor through worm reduction gearing. In certain cases, when drying fine powdery materials, greatly improved operation is obtained if provision is made for dealing with the dust rising from the scraper knives. In such cases an aluminium hood, completely covering the upper part of the cylinder and fitted with hinged inspection doors, is advisable.

**Evaporators.** The evaporation of liquids is an operation which is of frequent occurrence in the laboratory and a short note on an efficient apparatus for such work is indicated.

The term evaporation is applied in general to any process in which a liquid is converted into vapour. Vapour in an equilibrium condition above a liquid has a definite pressure increasing with temperature up to its boiling-point at which the pressure is then the atmospheric pressure prevailing. In order to increase evaporation or to reduce the boiling-point for sensitive liquids, the pressure may be reduced by condensers and vacuum pumps.

The early method of evaporation was by the application of direct heat applied to open pans either by an oven underneath or the use of hot flue gases, either around or above the pan, or by direct solar radiation. Steam is now almost the universal means of conveniently transferring heat for evaporative purposes. Its temperature can be controlled by the pressure in the boiler and subsequent use of reducing valves, e.g. at 100 lbs. per square inch its temperature is 170°. In this way an effective temperature drop can be obtained between the heating medium and many of the normal solutions to be concentrated.

In certain instances by the use of a stirrer, superheating is reduced and burning prevented. In the modified evaporator designed by Becker a thorough mixing of the evaporating liquid is secured without superheating by means of rotation, and a continuous film is drawn up on the side of the bulb and so an increased surface of liquid is obtained from which evaporation can take place. Four types of Becker's apparatus are shown in Fig 23 (VI), A, B, C, and D.

If a current of air be blown through the bulb, liquid may be heated much more strongly without the formation of bubbles. The air current may be produced in two ways: either by making use of the rotation of the bulb to eject the mixture of air and vapour centrifugally (Fig. 23 (VI), A), or by blowing in air directly by means of a filter-pump or bellows as in Fig. 23 (VI), B. When the bulb is revolved at a moderate speed (about

150 r.p.m.), the mixture of air and vapour is thrown out through the arms of the T by centrifugal force, and the air is consequently drawn in through the other end. In this way the escaping vapour forms its own blower, and materially hastens the evaporation.

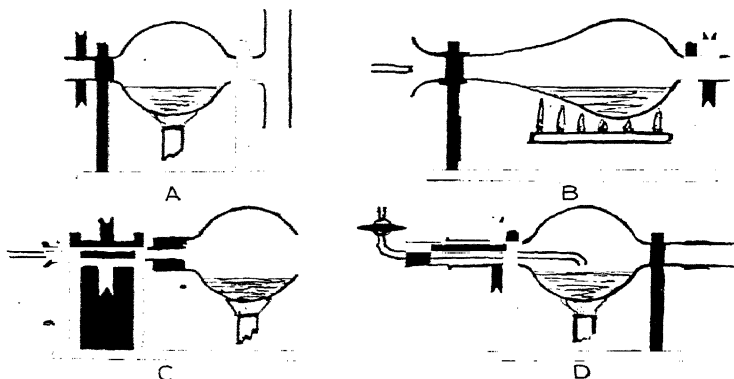


FIG. 23 (VI)

The latter method can be amplified further by supplying to the jet any particular gas in which the liquid under evaporation is most stable.

When the liquid has to be evaporated to dryness and the solid recovered, as in the determination of silica in analytical work or in the recrystallization of salts, a form of apparatus with a very wide opening at one end may be used (Fig. 23 (VI), c).

Owing to the complete absence of superheating, the apparatus in Fig. 23 (VI), D, is suited for use in evaporating at reduced pressure.

**Semi-Technical Scale Evaporation.**<sup>1</sup> The first application in evaporation with steam was by means of the jacketed pan, and later steam coils were introduced on the inside to give

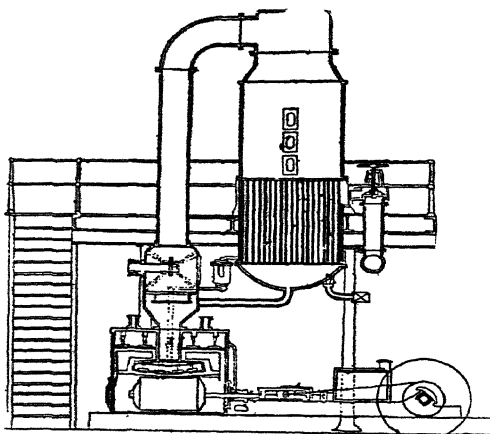


FIG. 24 (VI)

better thermal circulation of the liquid. The next important step was the introduction of the vacuum pan. This is of advantage where the liquor is

<sup>1</sup> Messrs. Kestner Evaporator and Engineering Co., Westminster, London, have provided the electros and have supplied data on technical scale evaporation and drying.

affected by temperature or if it has a high boiling-point. It also allows the use of exhaust steam and gives a higher temperature drop, thus increasing the rate of evaporation to some extent. A further development came with the introduction of the calandria pan. A typical installation is shown in Fig. 24 (VI).

The heating surface consists of a large number of short vertical tubes expanded into upper and lower tube plates. A large vapour space is arranged above the tubes to assist in separation of vapour from liquid and the vapour passes over into a jet condenser and wet vacuum pump. In modern types the design is improved by fitting one or more large diameter tubes near the centre of the tube plates, these acting as downcomers and improving the circulation round the tubes.

A higher efficiency in evaporation came with the introduction of the climbing film evaporator by Kestner of Paris. His inventions are embodied in the Kestner patent film evaporator, in which the liquid previously heated nearly to boiling-point is fed to the bottom of long vertical tubes. The general arrangement is shown in Fig. 25 (VI). On steam being applied to the outer surface ebullition at once takes place, releasing a volume of vapour which must find its way to a region of lower pressure by passing up the tubes. It carries with it a film of liquid round the inner surface of the heating tube, the mixture of vapour and liquid being separated in a tangential type separator at the top of the tube system. This type of evaporator gives a short time contact between heating surface and liquor, and may be used for sensitive liquors, and owing to the extremely thin film and its high velocity, optimum conditions for

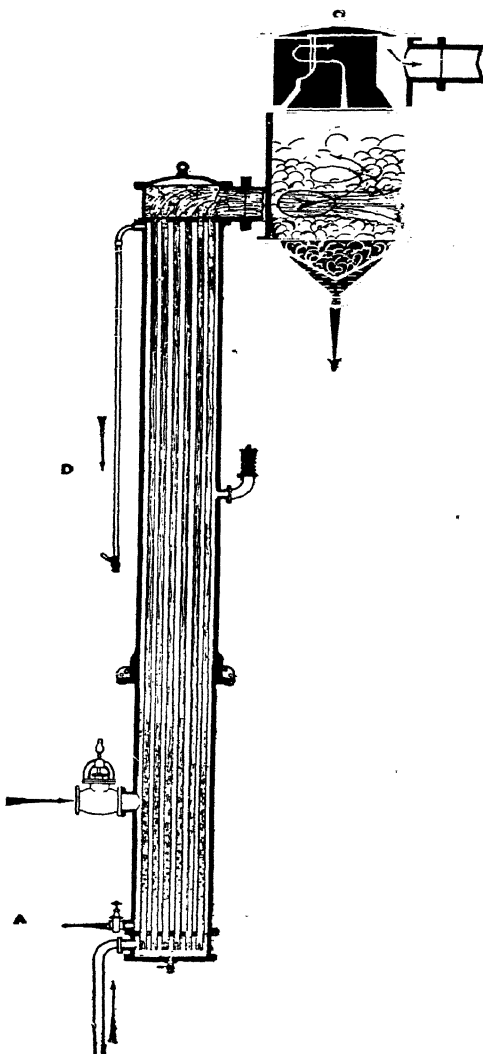


FIG. 25 (VI)

heat transfer exist. The high speed employed also reduces scaling to a minimum.

Fig. 25 (VI) shows an illustration of the standard climbing film type, but many different types are made to suit special conditions such as the falling film type, multi-circulation type, &c.

If the quantity to be evaporated is small a horizontal evaporator is often used. The liquid passes through several horizontal steam-jacketed tubes in series, at a high speed due to the vapour liberated, so that the advantages of the climbing film principle are maintained. The plant is very easily installed and may be conveniently placed against a wall, where it occupies very little floor space. It is widely used, for example, by manufacturing chemists and similar firms for the concentration of various extracts such as cascara, liquorice, &c.

Owing to the very large quantities of liquids to be evaporated in modern industrial and chemical operations, it became important to reduce steam consumption to a lower figure than that required for direct live steam evaporation. This was accomplished by the use of multiple effect evaporators. Steam applied to the first effect produces almost an equal amount of vapour which, in turn, can be used for the second effect, and so on. For example, in a single effect 100 lb. of steam will, under average conditions, evaporate 90 lb. of water compared with 250 lb. in a triple effect. Evaporation in successive effects decreases owing to radiation losses, and also due to the increase of latent heat of the vapour as the temperature decreases.

A certain temperature difference is required between each effect to give a reasonable heat transmission so that the number of effects possible is limited. The economic number possible is decided by a balance between capital cost and saving in steam consumption obtained.

An alternative method of evaporation and one working on an entirely different principle is evaporation in a current of hot air. One of the best methods of accomplishing this is by spray evaporation. The liquid to be evaporated is fed by gravity on to an atomizer of special design which consists essentially of a disc running at a high speed of 10,000 r.p.m. or higher. The liquid is broken up into a fine spray which is evaporated almost instantaneously in a current of hot air which is passed into the evaporating chamber through a specially arranged distributor at the top. With this construction difficulties with the choking of small jets and the maintenance of high-pressure pumps required by other systems are avoided.

The plant can be used either for concentrating liquids or for drying liquids to powder form. The temperature of evaporation for drying is low since it only reaches the point at which the vapour pressure approaches equilibrium with the partial pressure of the air leaving the plant. The system is accordingly particularly suitable for delicate products such as milk, fruit juices, &c. The hot air can be obtained from any convenient source, for example, by means of steam heating or direct-fired heaters using coal, oil, or gas.

Hot air is also used for evaporation in rotary-type driers which consist essentially of rotating cylinders inclined at a slight angle to the horizontal and fitted with different types of internal lifters. The liquid or slurry to be

concentrated or dried flows counter-current to the hot air, and the concentrated liquid or dried solid is discharged at the lower end.

An alternative type of continuous drier is the drum drier, which consists essentially of a rotating hollow steam-heated drum which dips into a trough containing the liquid to be dried. As the drum rotates it picks up the liquid on the surface and the dry solid is scraped off by suitable knives on the dis-

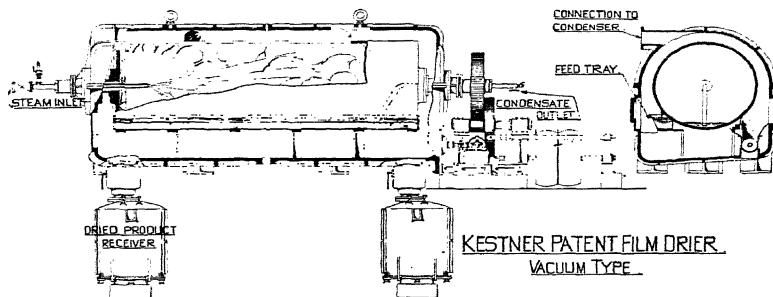


FIG. 26 (VI)

charge side of the drum. The machine either works under atmospheric pressure or can be enclosed in vapour-tight casing and operated under vacuum. Figs. 26 (VI) and 27 (VI) shows an improved drier of this type working under vacuum. The dry material is scraped off the drum by a series of knives of patented construction which prevent gradual building up of solids on the drum with consequent loss of efficiency.

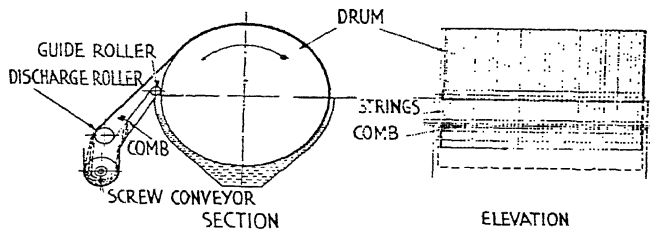


FIG. 27 (VI)

The above just outlines some of the principal types of evaporating and drying plant, but it should be emphasized that each problem must be considered on its merits, and the manufacturer should be consulted before deciding upon a plant for any particular purpose. The above plants are in the main designed for large-scale operations, but their use in pilot scale or even large-scale laboratory work may be possible in particular cases.



## SECTION 4: THE BALANCE AND WEIGHTS

**The Balance.** An accurate chemical balance consists fundamentally of a beam so constructed as to have the greatest possible rigidity consistent with

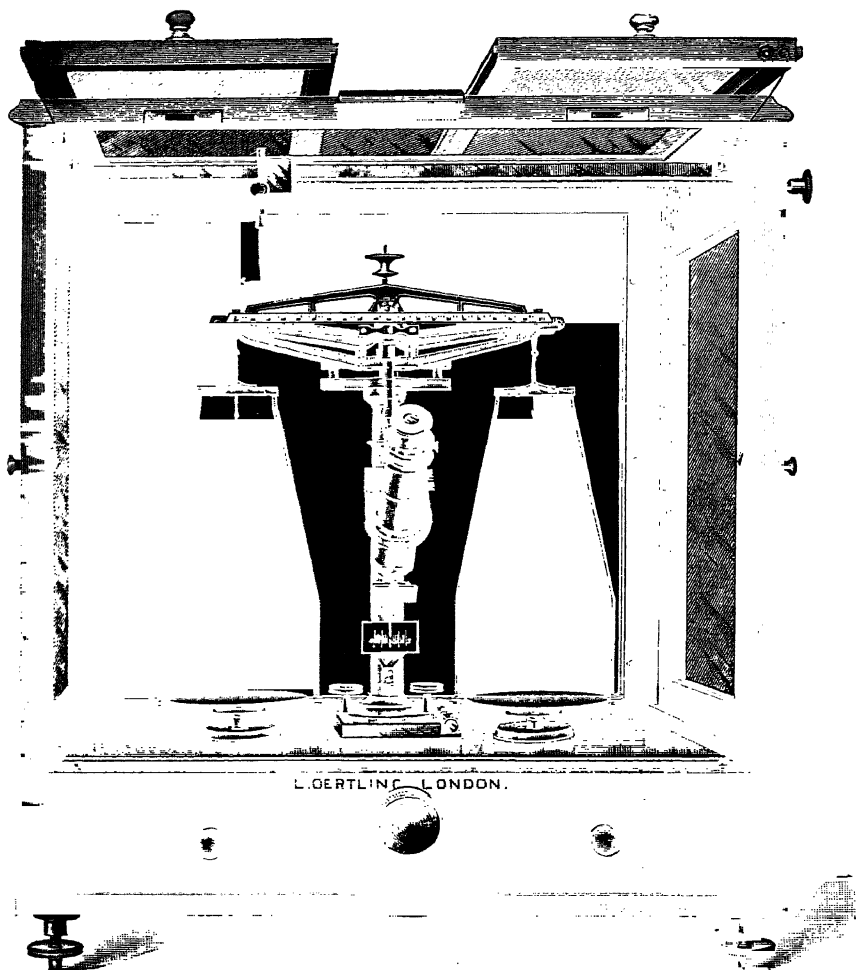


FIG. 28 (VI)

sufficient lightness, an alloy such as magnalium or the like being employed. This beam turns about a central point on a horizontal fulcrum or knife-edge, and carries at its ends two pans of similar material, on one of which, con-

ventionally that to the right, are placed the standard masses and on the other the body under investigation.

The figure (28 (VI)) shows a modern chemical balance suitable for practically all types of mass determination involved in physical chemistry.<sup>1</sup> The fulcrum of the beam consists of an agate knife-edge resting on an agate plane carried by a central pillar, while the two pans at either end are also suspended by knife-edges resting on planes of similar material; these knife-edges are attached to stirrups which, in turn, hold the pans. This balance will carry up to 250 grams in each pan and will turn with 0.1 milligram.

The state of equilibrium or otherwise of the beam is determined by the position of a long pointer so attached to the beam that it is vertical when the beam is truly horizontal. To facilitate these observations a scale is provided which may or may not be viewed by the aid of a microscope, according to the accuracy required.

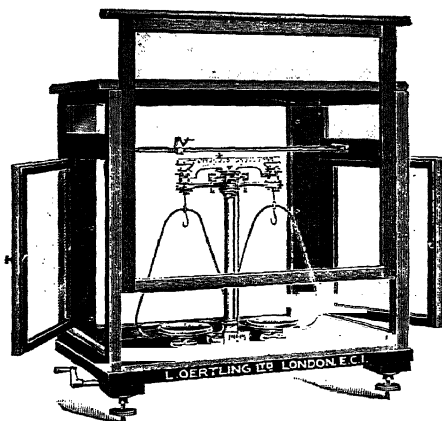


FIG. 29 (VI)

Another balance is shown in Fig. 29 (VI), and owing to its shorter beam has a quicker period, thus shortening the time of weighing. In the authors' experience the balance shown in Fig. 28 (VI) is probably slightly more accurate than that in Fig. 29 (VI), but slightly slower from the point of time of weighing. The beam carries up to 100 grams in each pan and turns with 0.1 milligram. It also has agate knife-edges working on agate planes. The need for a rigid table to support the balance in its case has been emphasized already. To lessen or absorb slight movements due to working of motors or machinery, the legs of the balance might be inserted partly in rubber supports, which act as shock absorbers.

### SENSITIVITY

The most important constant of a balance is its sensitivity, that is, the

increase to the deflection of the beam for a given small additional load on one pan. The expression sensitiveness is also used in the same connection. This may be determined as follows: In Fig. 30 (VI) let A and B represent the terminal points of suspension of the pans, let C be the middle point of the line joining them, and D the point of suspension of the beam. Also let

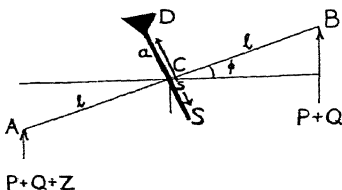


FIG. 30 (VI)

<sup>1</sup> Electros for Figs. 28 (VI), 29 (VI), 32 (VI), 33 (VI)—37 (VI), 40 (VI), 41 (VI), 45a (VI) and 46 (VI) kindly supplied by L. Oertling Ltd., London.

S indicate the position of the centre of gravity of the beam alone. Further, let the distance AB be equal to  $2l$ ,  $CD = a$  and  $DS = s$ , and let it be assumed that the distances  $a$  and  $s$  are very small compared with  $l$ , so that DC and CS may be taken perpendicular to AB.

Again, let the pans have the mass  $Q$  and be loaded, as shown, with masses  $P$  and  $P + Z$ , and let the resulting angle of inclination of AB to the horizontal be  $\phi$ ,  $Z$  and  $\phi$  being taken as very small. Let the mass of the beam alone be  $m$  and let  $g$  be the acceleration due to gravity. Taking moments about D,

$$mgs \sin \phi + (P + Q)g(l \cos \phi + a \sin \phi) = (P + Q + Z)g(l \cos \phi - a \sin \phi)$$

$$\therefore \tan \phi = \frac{lZ}{ms + a(2(P + Q) + Z)}$$

$$\text{since } a \text{ and } Z \text{ are very small } \phi = \frac{lZ}{ms + 2a(P + Q)}$$

$$\text{and the sensitivity } \frac{\delta \phi}{\delta Z} = \frac{l}{ms + 2a(P + Q)}$$

In the above discussion it has been assumed that all the knife-edges are horizontal and parallel, and that the arms of the balance are equal and invariable. In practice these conditions are very nearly realized, so we can at once deduce that the sensitiveness of a balance is increased by having a long beam, by reducing the mass of the beam, by making the distance of the centre of gravity from the central knife-edge small, and also by the use of a long pointer. The reason of this last is obvious. These conditions, while increasing the sensitiveness, at the same time increase the time of vibration of the beam and therefore the time occupied in weighing. This follows at once by writing the equations of motion of the moving system. In general, therefore, a compromise has to be made—some of the sensitiveness has to be sacrificed to reduce the time of swing.

In precision balances, one of the quantities above mentioned—namely, the distance of the centre of gravity below the central knife-edge—is made variable by means of the gravity bob, a nut with milled edges moving on a screw vertically above the centre of the beam and held in position when the required adjustment is made by a locking nut. As the gravity bob is moved up the sensitiveness and time of swing both increase, while if it is put up too high the equilibrium becomes unstable. With long-beam balances a time of vibration of about 60 seconds is convenient, whilst with short-beam balances it may be reduced to as low as 10 seconds. Variations in sensitiveness may also be achieved by means of a slider on the pointer of the balance.

To get the required length of beam together with proper rigidity, but yet without making the beam unduly heavy, a light framework is used instead of a solid bar; this is usually either triangular in shape or may take the form of a girder with a web of light bars. The use of very long beams is not now so popular as it was, because equal sensitiveness with a shorter time of swing can be secured with a short beam and a long pointer. It is recognized, however, that any slight errors in the adjustment of the knife-edges produce greater effects with short than with long beams; in fact, it was only by improving these adjustments that the short-beam balance became possible.

**Constructional Details.** The three knife-edges should be exactly

parallel, and in general are so arranged that they all lie in the same plane when there is no load on the balance. If the beam were perfectly rigid the edges would remain coplanar for all loads; in most balances this is not so, and the two end knife-edges fall below the central one for heavy loads. In some cases the beam as a whole may be rigid, but the end knife-edges are carried on light metal projections, which are more easily deflected.

It is sometimes arranged that the terminal knife-edges are above the central one for small loads; then, as the load is increased, the beam bends very slightly, so that the three edges become coplanar, and with still greater loads the terminal ones fall below the central one. The sensitiveness then increases with the load until the knife-edges are in the same plane, and then decreases, thus giving maximum sensitivity at medium loads. The arrangement has the disadvantage that unstable equilibrium is likely to result when the terminal knife-edges are above the central one.

The centre of gravity of the loads and scale-pans should always be vertically below the knife-edges; this result is attained by having a loose link between the stirrup and the scale-pan, and also by taking care to place the weights centrally on the pan. In some of the best balances the centre of gravity of the pan and its contents is brought below the centre of support as follows: Two knife-edges are provided at right angles to one another. One of these is the ordinary knife-edge of the beam, the other is usually of cruder construction and is made of metal. This gives a support as nearly frictionless as possible, with freedom in both vertical planes.

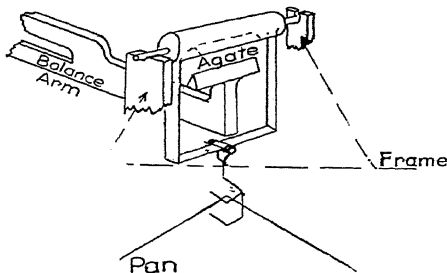


FIG. 31 (VI)

The method of fastening the knife-edges to the beam is important but will be considered here only briefly. Various devices have been used to ensure that the knife-edge and planes are always working in the same relative position—i.e. that release and arrestment do not interfere with their accuracy (Fig. 31 (VI)). Without considering in detail the subject of geometrical slides a reference may be made to the Kelvin 'point, line and plane' as an example. This device gives a constant relative position despite expansion. In some balances the point, line and plane are of metal, in the best they are of agate.

When not in use the pans of the balance rest on two supports, while the weight of the beam is also taken off the central plane and knife-edge. Mechanism is provided by which the weights of the beam and pans may be thrown on to the corresponding knife-edges and planes when required. At the centre the frame has two slots, which catch corresponding projections on the bar carrying the central knife-edge, while at each end are two screws with fine points, which engage respectively with a cone and slot on the stirrup which bears the agate plane and the pan. From the back of the plate fixed to the central column rises a short rod, to which is attached the horizontal rod bearing the central agate plane. This arrestment holds the

line fixed unless it is raised by turning a handle or milled head attached to a horizontal rod which bears two eccentric discs ; on one of these rests the end of the sliding rod or a small wheel attached to it, while the other eccentric operates the levers which raise or lower supports for the pans. Until the arrestment is released the central knife-edge is maintained just above its plane, and at the same time the end planes are clear of their knife-edges, the pans resting on the supports provided. Generally the handle for arresting the beam is in front, although in some balances not of the greatest delicacy it is very conveniently placed at the side to be operated by the left hand, leaving more space for the right hand to add the weights. The method described of raising the arrestment rather than the beam, which is sometimes employed, is much to be preferred : it makes it easy to start the balance swinging with a small amplitude and avoids disturbing the air in the balance case to any extent by the motion of the pans.

The pointer is attached to the centre of the beam and tapers to a fine point where it traverses the scale. Sometimes the scale divisions are carried to the top of the scale, and the end of the pointer then moves in the plane of the front of the scale and just over the top of it. Generally the fine end of the pointer moves over the front of the scale and very close to it to avoid parallax in reading its position. Another device consists of a small rectangular frame bearing a thin cross-wire and fastened to the end of the pointer ; the movement of the cross-wire is observed through a microscope fixed in the case. With the standard mark on the pointer the reading is dependent on the focusing of the microscope, and this restricts the range of swing. This difficulty is overcome in the following device for magnifying the range of the pointer. A micro-scale is mounted on the pointer upside down. This is observed through a microscope with a spider web in the eyepiece. A low-sensitivity balance with a microscope is preferred by most workers to the same balance adjusted to a greater sensitivity and without a microscope.

### THE RIDER

The rider is a small piece of wire having a mass of 1 centigram when the zero on the scale is at the centre (as in Fig. 28 (VI) ) and 5 milligrams when the zero is at the left (as in Fig. 29 (VI) ). In the last case the rider is always on the beam scale. Subdivisions of this mass are obtained by varying the distance of the rider from the fulcrum of the beam, it being moved to various positions on a rider scale fastened to the beam for that purpose. Some scales are divided into 100 rather than 50 parts. The top of the scale is best arranged so that it lies in the same horizontal plane as the three knife-edges. It is a common practice, however, to have the scale above this plane but parallel to it, or even to use the top bar of the beam as the scale, in which case the scale is often not horizontal. The effect of having the scale in a horizontal plane above the knife-edges is to increase the sensitiveness when the rider is put on, but the sensitiveness is not altered by moving the rider from one scale division to another. The effect can be nullified in such a case by placing the rider at the centre of the scale—i.e. directly over the central knife-edge, when it is not being used, instead of raising it off the scale, as is commonly done. In the last case, when the scale is not horizontal, when the beam is

at rest, the sensitiveness will rise as the rider is moved from the end of the scale towards the centre. The first arrangement is therefore preferable, because the addition or removal of the rider does not alter the sensitiveness. The effect is a small one, owing to the small mass of the rider, and is only important in very accurate work.

The rider is manipulated by means of a lever worked from outside the balance case by any suitable mechanism.

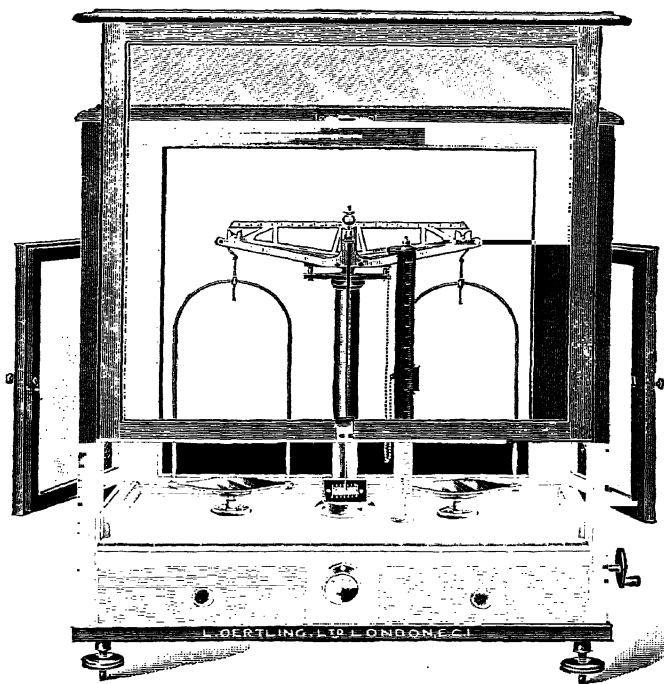


FIG. 32 (VI)

**Chain-Vernier Balances.**—To eliminate the use of small weights the so-called chain-vernier balance has been devised. In the Christian Becker type (made by Eimer and Amend, New York) <sup>1</sup> a gold side chain is fastened at one end to the right side of the moving beam of the balance and at the end to a slide arranged with a vernier. As this slide is raised or lowered the pull on the beam is altered, thus creating a series of different weights read from a scale on which the slide moves. The slide is operated by a thumb-screw from the outside of the balance so that weighing can be done with the window closed. Riders and small weights up to 50 milligrams are eliminated. Messrs. L. Oertling, Ltd., make a balance of this type (‘chainomatic’ system), see Fig. 32 (VI), and its mechanism is explained in Figs. 33 (VI) and 34 (VI).

<sup>1</sup> *Metallurgical and Chem. Eng.*, 1916, (4) 14, 230.

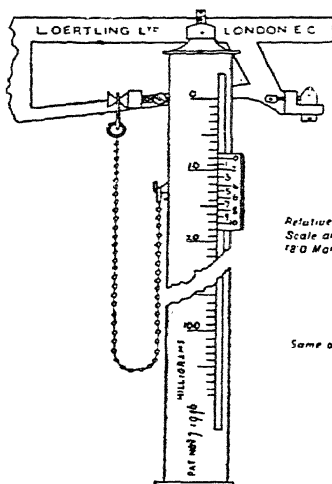


FIG. 33 (VI)

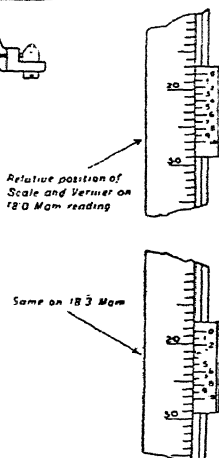


FIG. 34 (VI)

obtained by means of dash-pots supported on arms attached to the pillar of the balance. Attached to arms fixed on the ends of the beam are movable prisms, consisting of circular aluminium plates, having a slight clearance from the periphery of the cylinders. In each of these two plates is an aperture which can be covered completely or partly covered at will for the purpose of controlling the period of swing. It should be noted that the aperture is correctly adjusted by the manufacturers and should not be interfered with unnecessarily. This air-damping device brings the beam to rest quite rapidly without interfering in any way with the sensitivity of the balance.

**Prismatic Device.** (Fig. 36 (VI).) At the end of the pointer of the balance a transparent 'graticule' (or reading-index) is attached. This graticule is provided with a varying number of divisions according to the particular type of balance employed. A beam of light passes through an aperture at the base of the pillar on which the beam is supported, the source of light being obtained from a 12-volt projection lamp placed outside the balance-case behind the pillar, and by means of mirrors and prisms an enlarged image of the graticule is reflected on a ground-glass screen fixed to

## OTHER TYPES OF BALANCES

**The Prismatic Reflecting Balance.** The introduction of the aperiodic prismatic-reflecting balance marks a really great advance in precision balance design (Fig. 35 (VI)). This new type of instrument has been evolved as a means of providing the industrial chemist with a balance which saves a considerable amount of time in the mechanical operation of weighing and at the same time eliminates certain risks of error by the avoidance of the use of riders and small fractional weights.

### Constructional Details.

**Aperiodic Device.** This is ob-

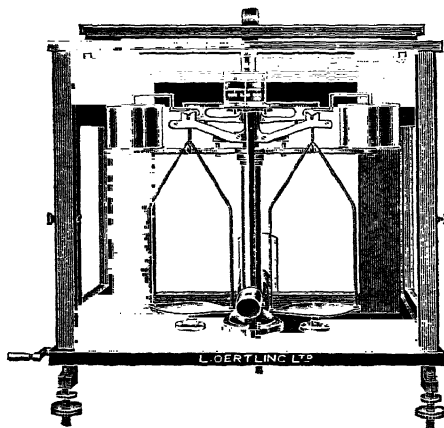


FIG. 35 (VI)

the top of the balance case, upon which is engraved a datum line. The illuminated screen is in line with the operator's vision and can be distinctly read to the fraction of a division, without difficulty.

In order to correct any slight change of rest-point, the screen is adjustable by means of a milled-headed screw placed outside the balance case, so that any zero error can be corrected without opening the case.

The principal divisions on the graticule are numbered from 0 on the left to 250, 500, or 1,000 on the right, according to the type of balance required. Graticules having a central zero for plus and minus weighings are also provided. The central zero, however, reduces the 'automatic' readings by one-half, e.g. a balance having the graticule with the left-hand zero will indicate differences in weight up to 50 milligrams with the '500'-division scale, *without* placing any weights in the right-hand pan; with the central zero the range would be reduced to 25 milligrams.

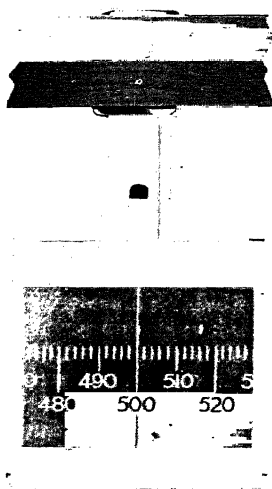


FIG. 36 (VI)

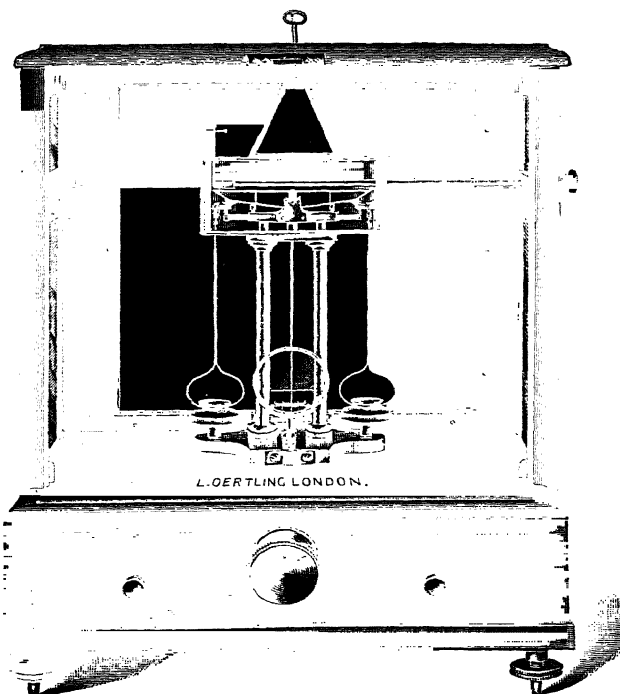


FIG. 37 (VI)

**The Assay Balance (Fig. 37 (VI).)** These balances have a maximum load of about 2 grams, and are sometimes sensitive to 0.01 milligram. They can therefore be used for accurate determinations of small weights. The same principles are used in the construction of these balances as in those for heavier loads, but since the loads are to be small, increased sensitive-



ness can be secured by making the parts light as far as is consistent with rigidity. Both short- and long-beam assay balances are made.

**The Cantilever Balance.** For the rapid and accurate weighing of loads of the order of a few milligrams to within 5 per cent of their weight an apparatus called the Cantilever Balance has been devised by the Research Staff of the General Electric Co., Ltd., London. It was employed by them with very satisfactory results to sort filaments for gas-filled lamps, of various sizes, ranging in weight from 8 to 30 milligrams, and will indicate with certainty a variation in weight of 0.1 milligram, which is a small difference for rapid weighing. As it illustrates a method of weighing differing in principle somewhat from that of the ordinary balance, a short description may here be given.

The arrangement is shown diagrammatically in Figs. 38 (VI) and 39 (VI). The body to be weighed is placed in the depressions provided in the fine steel wire cantilever A A, which carries a light mica vane to damp its vibration. The end P of the cantilever is deflected by the weight, and the move-

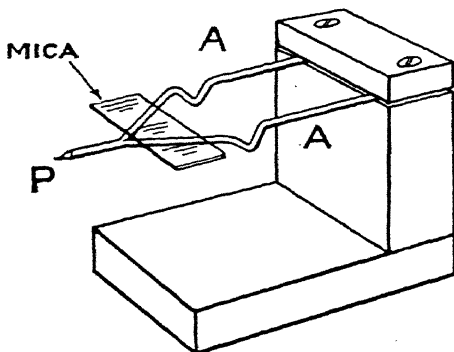


FIG. 38 (VI)

ment is magnified thirty times by an optical projection apparatus. This consists of a *pointolite* lamp, a condenser and a prism, which are used to illuminate P, and of a microscope of 0.7 inch focus which forms an image of P on the screen *s*. To shorten the apparatus and to bring the screen nearer to the observer, the light is again reflected by the mirror M. The screen is of semi-transparent paper on glass with a scale of milligrams marked on it, and the image of the pointer is observed through the paper.

The zero adjustment is accomplished by moving the screen and the scale.

The filament or other object to be weighed is lowered on to the cantilever; in actual use with a filament, a carrier C was provided. This carrier could also be used to remove the filament after weighing and deposit it in one or other of three boxes, B1, B2, B3, according to its weight. The speed of weighing and sorting with a balance previously standardized was about 400 filaments an hour.

In the above, the weight of the body under test is balanced by the resistance to loading of the material forming the cantilever. This furnishes an indirect comparison with standard masses, as the whole is previously calibrated with them. In the Nernst micro-balance (see below) the torsion resistance of a quartz thread is utilized to supply a comparison between the pull of the earth on the body under test and the standard masses. Another principle is involved in the Steele-Grant micro-balance also described. A number of other methods are also available, and besides those actually applied many others of theoretical interest would seem capable of application.

It will be observed that as most of these methods are indirect the apparatus employed requires previous standardization, and from this aspect

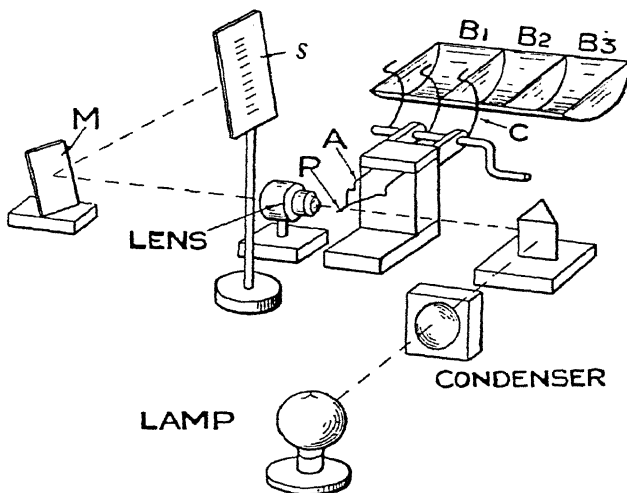


FIG. 39 (VI)

compares unfavourably with the ordinary lever balance which gives a direct comparison.

A new type of heavily damped balance using no loose weights of less value than 1 gram has been placed on the market by Sartorius-Werke, of Goettingen<sup>1</sup> (Fig. 40 (VI)).

The phosphor-bronze beam is of the straight Sartorius pattern with the usual type of supports, stirrups and arrestment mechanism. In place of fractional weights, eight separate riders weighing 500, 200, 100, 100, 50, 20, 20 and 10 milligrams are used. The riders, consisting of circular rings of wire, are placed on a notched rod which is attached to the top of the right-hand stirrup at right angles to the beam. Each rider has its own mechanism for lowering it operated by knobs placed vertically on the right hand side of the case. A half turn of any knob lowers the corresponding rider and at the same time brings into view a small indicator showing the value of the fractional weight used.

Weights of less than 10 milligrams are not used, but the sensitivity

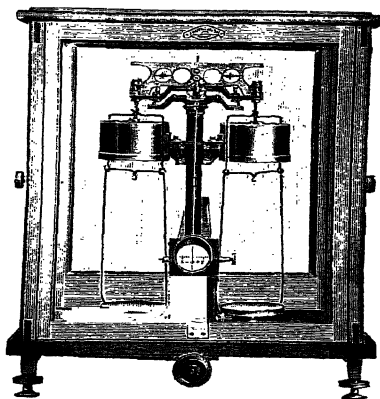


FIG. 40 (VI)

<sup>1</sup> Cocking, *J. Soc. Chem. Ind.*, 1931, 33, 696.

of the balance is so adjusted that each scale division corresponds to 1 milligram. By means of a small electric lamp placed outside the balance case, and a system of lenses and mirrors, an enlarged image of the scale is projected on to ground glass, and the image moves across the field as the pointer swings.

The damping device consists of a pair of very light aluminium cylinders, closed at the top but open at the bottom; these are suspended from the stirrups and fit loosely into a pair of brass cylinders, open at the top but closed at the bottom and fixed rigidly to the central support of the balance. The clearance between the aluminium and brass cylinders is about 0.0625 inch, and the damping is produced by the cushion of air inside the cylinders. The wires, by which the pans are suspended from the stirrups, are hinged so that the cylinders always remain concentric even when the weights are placed away from the centre of the pans. The efficiency of the damping is demonstrated by the fact that no matter what weights are on the pan, or whether they are in equilibrium, the beam supports may be lowered without any damage or even jarring occurring.

Weighings are carried out in the usual manner with the larger weights and the supports are lowered completely after addition of each weight. To use the fractional weights the case is closed, the beam supports are lowered, and the riders are added while the beam is free. The beam does not oscillate but swings slowly to the equilibrium position so that until the correct weight to 1 centigram is added, the scale remains at rest at a point outside the graduations. When the correct fractional weight has been added, the illuminated image of the scale moves slowly across the field and comes to rest in 13 seconds. The reading on the scale indicates milligrams and fractions of a milligram. The balance is easily sensitive to 0.1 milligram.

#### MICRO-CHEMICAL BALANCES

The interest which has developed during recent years in various industrial laboratories in micro-chemical methods, an interest which will become more widely extended when the great advantages of this method are more generally realized by chemists has necessitated the attention of manufacturers of precision balances being directed to the production of instruments capable of dealing with the extremely small quantities of material involved, being in the nature of about one-hundredth part of the normal and therefore requiring a considerably increased sensitivity. The usual micro-balance has a capacity of 10 grammes and gives direct readings to 0.01 milligram; with estimated readings, i.e. by optically 'splitting' the divisions viewed through the microscope, readings to 0.001 milligram are said to be obtainable. This, however, will greatly depend upon the stability of the 'rest-point' of the particular instrument in use.

An Oertling prismatic micro-balance is shown in Fig. 41 (VI). This balance gives direct readings to 0.001 milligram per division on the illuminated reading-index.

The ordinary Nernst form is sensitive to 0.001 milligram, while Steele and Grant describe one instrument for weighing 0.2 gram to 0.0001 milligram,

and another for detecting changes of weight of the order of 0.000004 milligram.

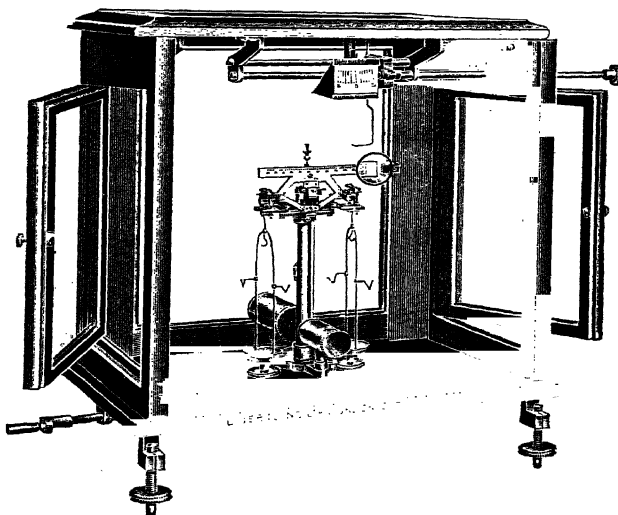


FIG. 41 (VI)

Nernst's micro-balance (Fig. 42 (VI)) has a bent glass capillary tube for beam. This tube is about 30 cm. long and 0.05 cm. in diameter; it is cemented at a point one-third of its length from one end to a fine quartz thread stretched between two metal prongs. It is therefore a torsion balance; the long arm is bent down at right angles and then outwards, and terminates in a fine point which moves over a graduated scale. The pointer is bent outwards at such an angle that if produced back it would pass through the point of suspension. The short arm has a platinum hook fused on, and this carries a small platinum scale-pan about 1 cm. in diameter. The weight of the scale-pan is balanced by a platinum rider cemented on to the other arm. The beam is raised from the arrestment in the usual way by a cam and thumbscrew. The scale can be calibrated with known weights and small objects can be weighed by substitution. The maximum load is 2 milligrams.

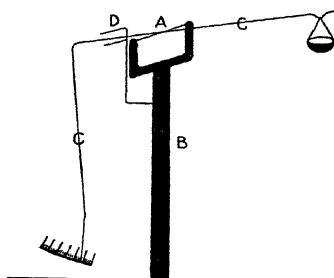


FIG. 42 (VI)

In the instrument described by Steele and Grant (Fig. 43 (VI)) the principle involved in weighing is as follows: A small quantity of air (0.01 milligram) is sealed in a quartz bulb; if the balance case contains air of the same density as the enclosed air (i.e. air at the same temperature and pressure) the apparent weight of the enclosed air will be zero, while if the

pressure in the balance case be zero the apparent weight of the enclosed air will be 0.01 milligram; the pressure can be read to one-tenth of a millimetre and can be varied from 0 to 760 mm., so that the apparent weight of the enclosed air can be varied by  $\frac{1}{10} \times 0.01 \div 760$  milligrams, i.e.  $1.3 \times 10^{-6}$  milligrams. This reasoning assumes that the beam of the instrument is homogeneous and that the zero remains constant, conditions which are found to be obtainable. The balance is made entirely of quartz, since this material combines lightness with strength, does not corrode, has a small temperature coefficient, and is only slightly hygroscopic; it can also be obtained in a pure condition and can readily be cleaned. The beam consists of a framework of quartz rod, is about 5 cm. long, and carries at its centre two small quartz knife-edges about 1 cm. apart and also a small mirror. A fixed counterpoise is attached to one end of the beam, and to the other is fused a fine quartz fibre 0.5 cm. long

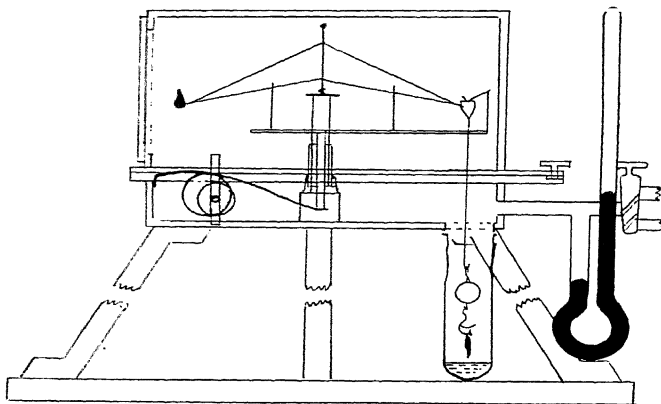


FIG. 43 (VI)

with a hook at its lower end to which is attached a short quartz rod, then a sealed-up quartz bulb, below this a quartz scale pan, and, lastly, one of a series of quartz counterpoises. In some forms the scale-pan, &c., are suspended by a knife-edge. The balance is contained in a small metal case with a plate-glass window in the end through which a beam of light can be thrown on the mirror and reflected back on to a scale.

The cover has a broad flange, ground to give an air-tight joint when lubricated, with a corresponding flange on the base. The beam arrestment is worked by means of a cam actuated by a thumbscrew outside; the axis of the latter is ground conically to fit a tapering brass tube made air-tight by lubricating. To the side of the case are attached a manometer and a two-way tap for exhausting. In the base, by means of a ground-glass joint, fits a glass tube in which hangs the scale-pan, &c. In weighing the rest-point is first observed, with no load on the pan and at some fixed pressure  $p$ ; the weight of air in the quartz bulb is known from the volume of the bulb (determined by weighing it full of mercury)

and the temperature and pressure of the air at the time of sealing it up. Suppose this pressure is  $P$  and the weight of air  $W$ ; now, with the load on the pan the pressure is adjusted to some value  $p^1$  which brings the beam to the same resting-point as at first; the weight of the substance in the pan is then  $\frac{W}{P}(p - p^1)$ ; e.g. if the weight of air in the bulb was 0.01 milligram and the pressure at the time of sealing 750 mm., while the resting-point was the same with no load and a pressure of 640 mm. and with the load at a pressure of 42 mm. the load would be—

$$\frac{0.01 \times (640 - 42)}{750} \text{ milligram}$$

i.e. 0.00797 milligram.

To weigh larger quantities the counterpoise below the balance pan is replaced by a lighter one of known weight (determined on the micro-balance itself) and the difference of the weights of the two counterpoises at the two pressures is added to the weight determined as above.

This balance was employed by Ramsay and Gray to fix the density of Radon (Niton), when the quantity of material available was about 0.005 milligram.

The most sensitive micro-balance is an electro-magnetic compensation balance, on the same principle as the Ångström balance designed by Emich, in which the current resistance through an electro-magnet is altered and weights compared by a millivoltmeter. The accuracy of such a balance is such that a difference in weight of  $0.015\gamma$  can be estimated where  $\gamma = 0.001$  milligram.

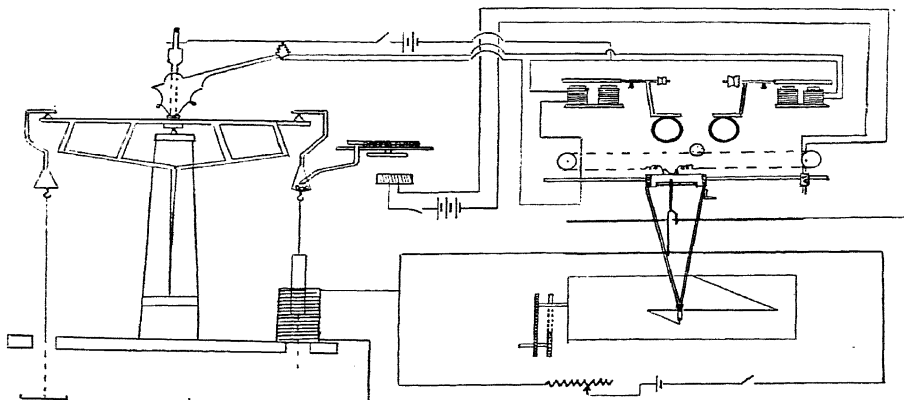


FIG. 44 (VI)

**Automatic Balance (Odén-Keen).** An automatic and continuous recording balance (Fig. 44 (VI)), which gives an accurate record of change of weight with time, has been described. It enables processes such as the evaporation of water from fibres to be followed without the repeated weighings which have hitherto been essential.

Control is effected electromagnetically. The current passing through a solenoid is automatically adjusted so that the attractive force on a magnet suspended from one pan of an analytical balance is just sufficient to maintain the balance in equilibrium. Adjustment of the current is accomplished by the movement of a sliding contact along slide wires, and this movement is in its turn controlled by the slight swing of the pointer attached to the balance beam as the latter moves from its equilibrium position. When the current and hence the weight on the second pan of the balance reaches a prearranged value a subsidiary circuit is automatically closed and a small phosphor-bronze sphere of known weight, about 0.5 to 0.05 gram, according to the conditions of the experiment, is deposited on the pan above the magnet, the sliding contact is drawn back to its initial position, and the cycle of operation recommences.

The arrangement of circuits is such that the distance of the sliding contact from its zero position is to a close approximation linearly related to the current. Hence a recording ammeter is not needed, as a record on a rotating drum of the slider position is sufficient to give the required data. The record so obtained consists of a series of stepped curves and a very open scale is obtained. Both slow and rapid changes in weight can be followed.

**Torsion or Spring Balances.** A rapid weighing lever balance of the automatic direct-reading type is extremely useful in a laboratory where a number of routine weighings are required. Two types might be required: a simple type like that employed for weighing postal letters and a more accurate type for micro quantities. Faberge<sup>1</sup> has devised spring torsion balances of the micro-type covering a range of 0.4 to 2.3 milligrams. The

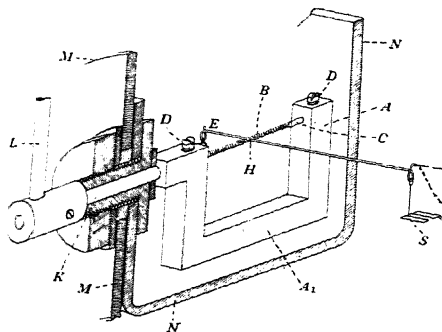


FIG. 45 (VI)

relative sensitivity is about 0.002 of the maximum load, while the absolute sensitivity attainable is at least 0.001 milligram by direct reading. Weighings can be made at a rate of about two per minute. A null method is used in the balance and the spring is helical and is stretched across a movable frame. This frame is rotated about the axis of the spring until the torque produced by the load is balanced, and the arm to which the load is attached is brought back to its initial position. In this case the spring acts as the sole support of the arm carrying the load, and the system is therefore frictionless, which enables considerably higher absolute sensitivities to be attained.

The principle of the balance is shown in Fig. 45 (VI), in which the movable frame A is used to stretch and support the spring B. The spring

<sup>1</sup> *J. Sci. Inst.*, 1938, 15, 17.

is attached at its ends to short wires C held in the frame by the grub screws, D, D, and the arm EF is attached at right angles to the spring at its midpoint H. A loop at the end F carries the free hanging 'pan' S on which the load is placed. At the other end is another loop at E to which a counterpoise, made of stout wire, is attached by a ring of fine wire (e.g. 48 S.W.G.). The end of the arm F beyond the loop is drawn out to a fine point which faces a fixed point; these points are to enable the zero position of the arm to be observed.

The frame A is attached to the end of a spindle K, which passes through a moderately tight bearing and can be rotated by the arm L. Initially, when there is no weight on the pan, the side A<sub>1</sub> of the frame A is situated just above the arm EF so that the frame can be rotated counter-clockwise through the greater part of one revolution before it will foul the arm, thus twisting the spring and producing the torque required to balance the clockwise torque given by the action of the load on the pan. For details of working, &c., see original (l.c.).

In one example where the total range is 0.42 milligram the stretched spring is 16 mm. long and 0.9 mm. outside diameter and has 40 turns of wire of 0.023 mm. diameter. The torsion arm is 35 mm. long and is fixed at the middle point of the spring.

The behaviour of a helical spring (of circular cross-section wire) which is twisted axially and allowed to expand or contract freely in the direction of its axis can be expressed as

$$\phi = \frac{64MR}{d^4} n \sec \alpha \left( \frac{2 \cos^2 \alpha}{E} + \frac{\sin^2 \alpha}{N} \right)$$

where  $\phi$  = the angle of deflexion in radians  
M = the axial torque  
d = diameter of wire  
R = radius of coil  
 $\alpha$  = angle of plane of coil on axis of helix.  
n = number of turns in spring  
E = Young's modulus  
N = modulus of rigidity

Neglecting the sag, the spring of the balance can be regarded as consisting of two coils, one twisted and the other untwisted, obeying the above relationship.

For a spring of the dimensions considered  $\sec \alpha$  will change from 1.00995 to 1.00903 over one whole turn in each half of the spring—a difference which is very small, and which is in any case almost entirely cancelled by the fact that one half-spring is twisted while the other is untwisted. The term in brackets may also be considered constant. Therefore, for all practical purposes, the scale may be regarded as linear; this fact has been verified empirically. Consequently for calibration it is only necessary to fix two points on the scale.

Of the two balances made, one has been in use for 1½ years, the other for 2½ years. There has been no perceptible change in calibration over that period, although both balances have been transported in railways with no



other precautions than wedging the torsion arm. The zero needs adjusting from time to time, about twice a day if the balance is used continuously.

In weighing a large number of objects such as etherized *Drosophila*, a rate of about 30 seconds per weighing could be kept up for a few hours.

It may be noted that no special difficulties were encountered in making the more sensitive of the two models; it is thus not improbable that considerably greater absolute sensitivities than 0.001 milligram could be attained by the use of finer wire.

Sayre and de Forest<sup>1</sup> have studied the various errors in spring balances and have designed a new type of helical spring with an error of less than 0.05 per cent. Variations in temperature are eliminated by the use of a special alloy of a modified elinvar type. 'Back error' or hysteresis is less than 0.04 per cent. The load-deflection curve only deviates very slightly from a straight line and formulae for the curve have been developed.

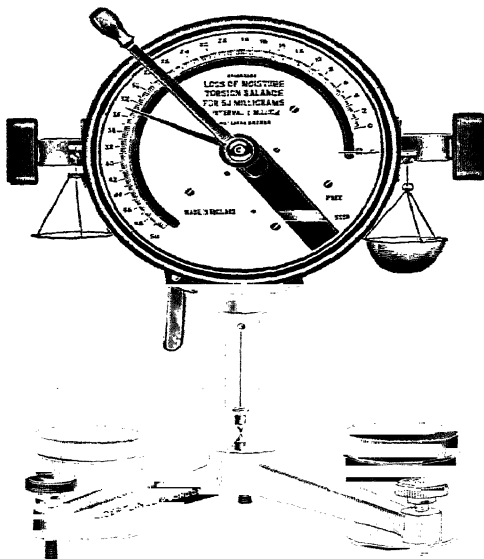


FIG. 45a (VI)

Oertling torsion balance used to ascertain the loss of moisture from substance. The balance beam is provided with two 'arms', the object to be weighed is counter-poised by weights and the loss of weight through evaporation is read on the dial. It has a range of 50 milligrams with a capacity of 5 grams and a sensitiveness of 0.1 milligram.

### CONSTRUCTION OF WEIGHTS

Before discussing the standardization of weights in detail some space may be devoted to a consideration of their construction. Those employed in physical chemistry are usually made in sets containing brass weights of from 50 grams down to a rider weighing 1 centigram, enclosed in a suitable wooden box lined with velvet. To preserve the weights from injury each has a separate compartment provided for it (Fig. 46 (VI)). Bakelite moulded weight-cases are also available.

As a material for the construction of weights brass is not ideal since it tarnishes easily, especially in the atmosphere of a chemical laboratory. It is, however, relatively cheap. Further, it is of sufficient density to render the masses usually employed in physical chemistry of suitably small bulk, and

<sup>1</sup> *A.S.M.E. Trans.*, 1936, 55, 379.

the correction necessary for the buoyancy of the air minute, except in very accurate work. Platinum is suitable but is costly; a compromise may be effected by coating brass weights with it. Such coated weights remain constant in mass over long periods, but they are not suitable for use as other than working standards; the fundamental standards must be constructed of platinum-iridium alloy. A large number of other materials have been suggested for use for laboratory weights.

Weights below 1 gram are usually made of platinum, gold, or aluminium.

The shape of the standard masses is a matter of practical importance; those above 1 gram are practically always made cylindrical in shape with a small projection on top for manipulative purposes. It may here be emphasized that on no account must scientific weights be handled, as this is certain to contaminate them with foreign matter; they must be moved

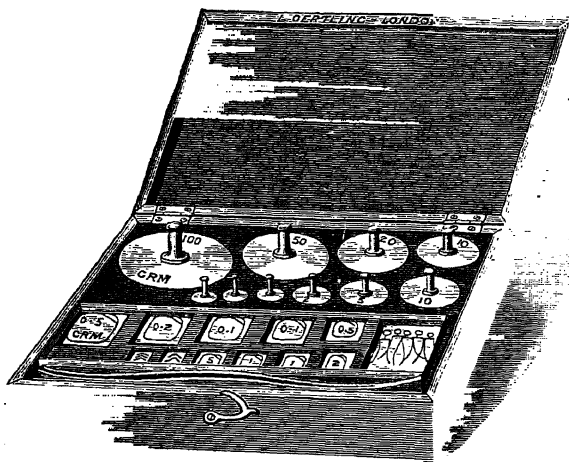


FIG. 46 (VI)

with the aid of a small forceps, preferably of the same material as that with which the weights are coated.

The smaller weights are made as flat sheets with a small turn-up for the purposes of manipulation, unless they are to be used as rider weights (see earlier), when they take the form of an arch-shaped piece of wire. The values of the weight in grams are usually stamped on them. The small flat weights are sometimes made of a definite shape, according to their value, for example, the 50 and 5 centigram weights are made hexagonal, the 20 and 2 centigram weights square, and the corresponding 10 and 1 centigram weights triangular. It is doubtful if this is of any real utility, as with a little practice the value of a weight is apparent from its size at a glance.

The standardization of weights is considered in Part I, Chapter II, Section 5.

## SECTION 5: ACCUMULATORS

Seventy years ago Planté made the first lead accumulator. In his cell two lead sheets separated by rubber strips and rolled into a cylinder were immersed in dilute sulphuric acid. Planté charged his cell by means of current from primary units. The cell had an E.M.F. of about 2 volts. Its capacity was built up by the following series of operations: (1) charge, (2) discharge, (3) recharge, but with the charging current entering in the reverse direction, (4) again discharge, &c. The effect of this cycle, known as 'formation', was to increase the available surface of the electrodes. Formation was a tedious and expensive process, occupying about two years.

Any plate on which the active material is formed by electrolysis from the plate itself is called a 'Planté' plate.

In 1881 Fauré obtained increased capacity and rapid formation of active material by the following innovation: he pasted the lead plates with red lead ( $\text{Pb}_3\text{O}_4$ ) which was more easily converted to spongy lead and fine lead peroxide by electrolysis. However, the active material derived from pasted materials broke away from the plates easily. Even down to the present day, the characteristic feature of any special unit is the manner in which the active lead and lead dioxide coatings are retained at the plates. The variety of methods used indicates the absence of any wholly satisfactory process.

Volckman introduced the use of lead plates with perforations containing pulverized lead.

The Brush and the Correns grids were the earliest examples of lattices or meshworks to hold active compounds.

The grid of a plate is the frame supporting active material. The positive plate of a charged or semi-charged cell has a covering layer of  $\text{PbO}_2$ . Lead dioxide has a resistivity of 76 ohms per ml., a value about 300,000 times that of pure lead. Hence the lead grid must be interwoven with the active material so that the compound plate transmits current evenly and readily.

Most manufacturers make positive grids of an alloy of lead with 7 per cent antimony. This alloy is less reactive than pure lead and is not weakened by acid corrosion. Also, antimony alloys expand on solidification and give sharp castings; this property is useful in the manufacture of grids with finely-worked crevices for loose active materials. Again, an electric current heats a conductor and increases its volume. The antimony alloy has a lower coefficient of expansion than has lead. Hence, mechanical weakening due to uneven expansion is minimized.

In the modern form of the Fauré pasting process litharge ( $\text{PbO}$ ) and red lead ( $\text{Pb}_3\text{O}_4$ ) are made into a stiff paste with sulphuric acid. Lead sulphate and dioxide are formed and the mixture cements. The firm paste is applied to the grids which are dried.

The details of the formation process do not concern us. A negative plate is produced by charging and discharging one of these pasted plates against a dummy positive or against another pasted plate, which becomes a positive finally.

The modern formation process lasts a few days.

The spongy plate of a negative plate is more conducting than the fine lead dioxide of a positive; also, the positive grid is subject to local action due to the contact: lead-lead dioxide. Hence, the negative grid is usually lighter than and needs less attention as to uniformity of current than the positive. The more vulnerable positive plate varies from cell to cell.

The commonest Planté positive is a lead sheet with grooves or leaves for lead dioxide. Planté plates are larger and heavier than pasted plates and have a relatively smaller capacity. They are used in stationary batteries in which durability is more important than space or weight.

In the rosette positive, rosettes or small rolls of corrugated lead tape are placed in holes in a plate, the latter being 0.4 inch thick. The corrugated rosettes are converted to chloride, then to dioxide. Formation causes expansion and firm wedging of rosettes.

The Planté negative consists of a perforated lead plate having a grid cast on one side. The pockets of the grid contain pulverized lead. A similar plate is placed over this one so that the ridges of the grids coincide. The leaves are then riveted to form a secure, though heavy, negative.

Pasted negatives, that is negatives of the Fauré type, are used for most cells. Batteries for lighting and starting vehicles (trams and motors) have pasted plates only.

A supporting rectangular grid is commonly used as a basis for the paste.

The Tudor accumulator, suitable for lighting and for any plant in which large capacity and high efficiency are needed, has an ordinary Planté positive and a two-piece pasted negative.

The Exide Ironclad battery is used in locomotives, trucks, tractors, cranes and wherever heavy duty and great vibration are incurred. The positive contains a number of antimonial lead rods clamped vertically.

In an ordinary cell the positive plates are arranged with faces parallel, the projecting lugs being fused to a cross-strap of lead which contains the positive terminals. The negatives are similarly bridged and are interleaved with the positives.

When two electrodes are conducting current, it appears that most of the current flows between the proximate faces of the electrodes. This means that the two different faces of the same plate are subject to different electrical and heating conditions. Now unsymmetrical expansion disintegrates a plate and the more fragile positives must be protected from one-sided flow of current. The electrical condition of the two faces of a positive are equalized by having negatives on both sides of *every* positive. This state of affairs is effected by having negatives at both ends of the interleaved row of plates.

Between each pair of neighbouring opposite plates there is an insulating separator. Glass lattices, sieves of hard rubber, wooden boards or perforated celluloid sheets are used as separators. These insulators prevent short-circuiting due to buckling or sprouting of the plates.

The Wildermann separating-frame is of porous ebonite. It permits free diffusion within the cell and lessens those differences of concentration which cause E.M.F. to vary.

The container of the cell is usually of rubber, celluloid or lead-lined wood; glass is best for radio low-tension units. The electrolyte is dilute sulphuric acid. Stationary batteries of low discharge rate have 30 per cent solution of density 1.2. Portable batteries of high discharge rate have 35–40 per cent acid.

On account of the deleterious action of impurity, distilled water and pure brimstone acid are used. The following are typical examples of the effect of impurity:

Vinal and Altrup found that one part of platinum in 10 million parts of electrolyte increased local action by 50 per cent.

Again, the potential difference between the plates of a charged accumulator is greater than that required for the decomposition of the electrolyte with evolution of hydrogen and oxygen. However, even though the necessary E.M.F. is present, electrolysis, that is self-discharge, does not occur. The explanation is that the surfaces of the Pb and PbO<sub>2</sub> have a peculiar tendency to retain any hydrogen and oxygen formed. Electro-negative metals like lead and copper destroy this passivity and with it over-voltage. The result is self-discharge on standing.

Manganese deposits in the pores of the plates and causes waste due to gassing as the plates are formed.

Lead accumulators are subject to three types of local action:

(1) Local action at the positive plate because of contact between the lead dioxide and lead. Ordinarily, the lead sulphate coating of the discharged positive is a protection. However, in roughly handled cells, the grids may be eaten away through this type action.

(2) Local action at the negative plate due to the deposition of metals more electro-negative than lead.

(3) Local action due to difference of acid concentration in the pores of the plates.

In considering the charge and discharge of a cell, we will concentrate on the following factors: maximum rate of working; capacity at various discharge rates; efficiency; and finally length of life.

For each make of cell there is a normal maximum discharge rate. Abnormally high discharge is bad; it cuts down capacity.

If a cell be discharged in normal time—10 hours, say—the voltage must not fall below 1.8. At a 1–2 hour rate, 1.75 volt is permissible.

Low voltage indicates that the acid in the pores is not being renewed fast enough.

If the cell be discharged below 1.8, sulphate cannot be formed within the pores for want of acid. The new reaction necessitated is often irreversible and destroys the life and constancy of capacity of the cell.

The capacity of a cell is obtained by allowing a regular current from the cell to traverse an ammeter or a copper voltameter until the E.M.F. of the cell decreases to 1.8 volt.

Current in amperes  $\times$  time of discharge in hours = capacity in ampere-

hours. The capacity of a cell varies with rate of discharge. Slow discharge means large capacity. (For measurement of efficiency, see later.)

**Care of Lead Accumulator.** (1) Use only pure brimstone sulphuric acid of specific gravity 1.20–1.21. If cell loses water by evaporation add distilled water till specific gravity is of proper value. If acid be lost by frothing, make up electrolyte to required concentration. Test specific gravity with tube or bead-hydrometer.

(2) Never discharge cell below E.M.F. of 1.85. 1.8 volts is permissible for special rapid-service cells.

(3) Do not leave cells discharged.

(4) Make periodic examination of cell. Remove side-growths, which might short-circuit.

(5) A weak cell may recover if kept off discharge for some days (charged). A weak cell is 'protected' in working if put in series with a good cell.

Abnormal loading of a cell produces buckling, growth and disintegration of the plates. Sulphating—the deposition of a scaly covering of hard sulphate which the charging-current only partially removes—may be corrected by the addition of some sodium sulphate to the electrolyte.

Disintegration due to local action cannot be cured.

High discharge rates are less harmful than improper or delayed charging.

A discharged cell has the following characteristics (besides low voltage, which may be detected with a voltmeter):

Positive plates dull red with pale patches. Negative plates dark grey and patchy. Positive and negative plates not readily distinguishable.

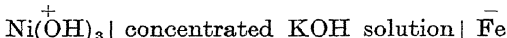
Signs that a cell is full-charged: Positive plate dark chocolate; at a short distance it appears black and glistening.

Negatives even, light, chalk-grey; no patches.

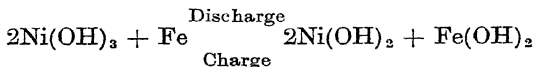
Gassing from both plates.

On standing for some little time the positives go chocolate-red or plum colour and the negatives lose their chalky look, going slate-grey.

**Alkaline Batteries.** In the Edison accumulator or cell the electrochemical system in the charged state is represented diagrammatically as follows:



When the cell is discharged the nickel hydroxide  $\text{Ni}(\text{OH})_3$  is reduced to the lower hydroxide,  $\text{Ni}(\text{OH})_2$ , and the iron is oxidized at the same time to ferrous hydroxide  $\text{Fe}(\text{OH})_2$ . On charging the reverse actions take place. The cell reactions are therefore



The electrolytic concentration is usually about 21 per cent KOH (S.G. 1.21) and this concentration remains practically constant during charging and discharging. The E.M.F. is practically independent of the electrolytic concentration within a wide range. Its value is 1.33 to 1.35 volts.

**Construction of Edison Battery.** Fig. 47 (VI) shows a positive plate. The nickel hydroxide is loaded in layers, in 0.25 inch perforated tubes (Fig. 48 (IV)) formed of spirally wound steel ribbon. Alternately with the

layers of nickel hydrate, layers of pure nickel flake are introduced to increase the electrical conductivity. When loading, the tubes are reinforced by eight seamless steel rings equidistantly spaced. Thirty tubes, properly clamped on the steel supporting grid, make an exceptionally strong positive plate. The negative plate (Fig. 49 (VI)) contains iron oxide as active material. Mixed with a little mercury oxide to increase the conductivity, it is loaded into perforated, rectangular, sheet-steel pockets and solidly tamped down. Twenty-four finished negative pockets are inserted into each negative plate and each pocket case is perforated with approximately 560 holes to the square inch. When loaded, the pockets are placed in the interstices of the steel supporting grid and forced between corrugating dies into perfect electrical contact. The operation is carried on under a hydraulic pressure of 120 tons and this flanges the pockets out over the sides of the grid and

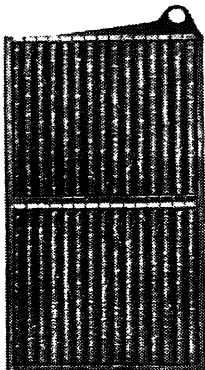


FIG. 47 (VI)



FIG. 48 (VI)

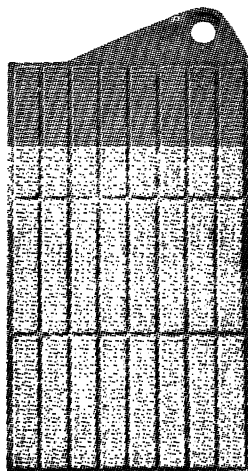


FIG. 49 (VI)

corrugates their surface. The plates are set in steel rods which are inserted in holes at the top of the plate frames with washers between the plates. The complete set of positive and negative plates are intermeshed and separated by hard rubber rods or pins. Thin rubber sheets are also used to insulate the plates from the nickel-plated steel container.

The average working voltage of the Edison accumulator is 1.2 volts per cell at the normal or 5 hours rate of discharge. At lower rates the value may be increased to nearly 1.3 volts per cell.

Fig. 50 (VI) shows a typical voltage-time curve for charging and discharging, taken at normal rate. At the beginning of the charge the voltage across the terminals is of the order of 1.55 volts. This will rise gradually to a figure of 1.84 volts, at which it remains steady. From the start an evolution of hydrogen occurs at the negative plate. At the start no oxygen is evolved on a positive plate but does so actively before the end of the charge.

The ampere-hour efficiency of the cell is lower than that of the lead

accumulator, but depends on rate of charge and discharge. The lower these are the higher the efficiency. The normal efficiency is about 82 to 85 per cent, and the watt-hour efficiency about 59 per cent.

There are many modifications of the original Edison accumulator. For example, in the Ionic cell pure graphite is used in place of flake nickel and also cadmium-iron negative plates. In the Jungner cell the negative plate is a cadmium-iron mixture with approximately 80 per cent. of cadmium and graphite is used in the nickel hydroxide positive paste to increase conductivity. A more recent accumulator of the alkaline type is found in the Drumm battery. The positive plate of this battery is identical with those used in the standard Edison cell and the novelty is in the negative plate.

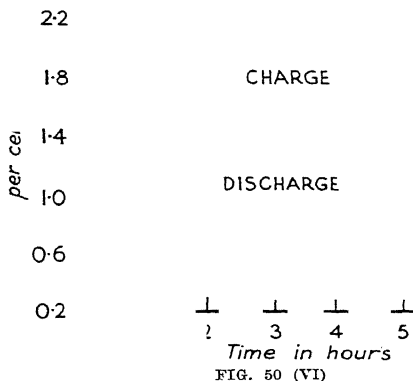
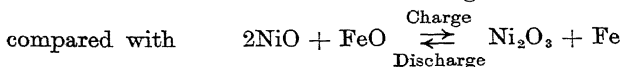
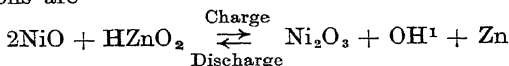


FIG. 50 (VI)

*The Drumm Battery.* The Drumm negative plate consists of a Zn — Zn(OH)<sub>2</sub> system. On discharging a Drumm cell the zinc metal plated out on its negative plates during a previous charge is converted into zinc hydroxide, the latter dissolving in the potassium hydroxide solution constituting the cell electrolyte. In the latter respect the Drumm cell differs markedly from the Edison cell, for on discharging an Edison cell the metallic iron powder constituting its negative plates is converted into Fe(OH)<sub>2</sub>, which is insoluble in the alkaline cell electrolyte.

On charging an Edison battery the solid hydroxide becomes reduced to metal. In the Drumm battery, in its final forms, the negative plates consist each of corrugated sheets of solid nickel of special purity. On charging such a cell, zinc metal is plated out of the cell electrolyte on to the nickel negative plates. The cell electrolyte consists of a solution of 5 per cent zinc hydroxide dissolved in 21 per cent caustic potash.

The cell reactions are



in the Edison nickel oxide iron accumulator,



On account of the relative position of zinc and iron in the electrochemical series, and also due to its low internal resistance, the average discharge voltage of this zinc accumulator is high (1.68 compared with 1.20 for its iron analogue).

Like the Edison battery, the Drumm battery has now been proved to have a service life of 10 years. The Drumm battery can yield exceptionally heavy currents both on charge and discharge. Such heavy currents do not adversely affect its guaranteed life.

The average current efficiency of a Drumm battery is 84–85 per cent; the average charging voltage is 2.0, and the average energy efficiency 72–73 per cent. All the foregoing figures hold good for very high rates of working both on charge and discharge. The maximum output per single discharge for the commercial forms of Drumm battery is 10 watt hours per lb. weight of complete battery.<sup>1</sup>

**Efficiency of an Accumulator.** The efficiency of an accumulator may be expressed in terms of the quantity of electricity and of electrical energy. The quantity of electricity is measured in coulombs (amperes  $\times$  seconds), the electrical energy is expressed in watt-hours (watt-hours = amperes  $\times$  volts  $\times$  time hours.)

$$\text{Ampere-hour efficiency} = \frac{\text{Coulombs obtained on discharge}}{\text{Coulombs required for charge}}$$

$$\text{Watt-hour efficiency} = \frac{\text{Watt hours obtained on discharge}}{\text{Watt hours required for charge}}$$

The quantities required for the measurement of efficiency are, therefore, the current strength, the potential difference, and the time. Fig. 51 (VI) illustrates a convenient method for measuring these quantities and so determining the efficiencies.

(1) *Ampere-hour Efficiency.* For charging, the discharged accumulator

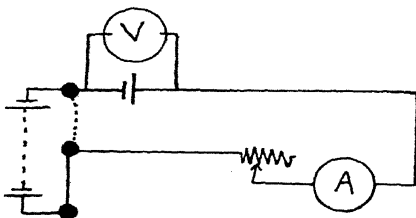


FIG. 51 (VI)

is inserted as shown. The key of the charging source is closed and the rheostat adjusted so that the current assumes a suitable value (usually about 1.5 amp.). The exact time of switching on is noted, and the charging continued until there is a vigorous evolution of gas. The charging current is maintained constant during the charge. The ampere

hours taken on charge are then equal to current  $C \times$  time  $t$ . The key is now thrown over and the rheostat adjusted, so that the discharge current is the same as the charge current. The discharging is continued until the voltage of the cell as measured by the voltmeter across its terminals begins to fall below 1.8 volts. The time of discharge is then noted and

$$\text{Ampere-hour efficiency} = \frac{Ct_1}{Ct} = \frac{t_1}{t}$$

<sup>1</sup> See *Modern Transport*, XLII, No. 1073, 1939, for reference to a large Drumm Battery of Ampere-hour efficiency of 90–93 per cent and Watt-hour efficiency of 70 to 74 per cent.

(2) *Watt-hour Efficiency.* The watt-hour efficiency may be obtained by reading every 15 minutes, the voltmeter across the terminals, during the charging and discharging processes. Time-potential difference curves for the charging and discharging are then constructed. If the current strength has been constant and the same in both cases, the ratio of the two areas is equal to the ratio of the energy taken out, to the energy put in and gives the watt-hour efficiency of the cell.

#### OTHER EQUIPMENT

In this chapter the laboratory equipment considered has been restricted to such items as thermostats, stirrers, drying and evaporating apparatus, balances and weights, and accumulators. In the next chapter various forms of circulating and compression gas pumps are described. With regard to other apparatus it is considered throughout the book according as its employment is necessary, e.g. various types of apparatus for measuring temperature are considered in the chapter on Thermometry, high pressure equipment is reviewed in the Chapter on High Pressure Technique, and optical instruments under Spectroscopy, &c., in Volume II. The construction of instruments and apparatus and a review of the materials required in research are the subject-matter of two sections in Strong's <sup>1</sup> *Procedures in Experimental Physics*.

<sup>1</sup> Prentice-Hall, N.Y., 1938.



## CHAPTER VII

### PUMPS

#### SECTION 1: CLASSIFICATION OF PUMPS

**A** PUMP may broadly be defined as an apparatus for transferring (either partly or wholly) a liquid or gas from one vessel to another and thus producing a difference of pressure between them.

The physical chemist is, generally speaking, not concerned with liquid pumps except in so far as they are used for producing a circulation or mixing effect as a subsidiary operation. The mechanism of such pumps being simple and usually similar to that of one or other of the gas circulation pumps described in this chapter, it is not proposed to treat of them specially.

#### CLASSIFICATION OF GAS PUMPS

For convenience gas pumps may be classified according to the following scheme :

- (a) Circulation pumps, for producing pressures not far from atmospheric.
- (b) Compression pumps, for producing pressures above atmospheric.
- (c) Exhaust pumps, for producing pressures below atmospheric.

This classification is quite arbitrary, and has no reference whatever to the mechanism of the various pumps described. In fact, to a certain degree, practically every type of pump can function in any one of these three classes.

#### CIRCULATION PUMPS

Circulation pumps for laboratory use do not as a rule require to be designed with a view to obtaining the greatest efficiency, since leakage is usually unimportant and the order of pressures involved small. As a rough approximation it may be said that the difference between the compression and exhaust pressures is in the neighbourhood of half an atmosphere. Large numbers of such pumps have been designed from time to time to meet special needs ; those described in this chapter may be taken as typical.

**The Piston Pump.** This type is illustrated in Fig. 1 (VII) (a). The essential parts are : the outer casing A, the piston B, piston shaft C, and the valves F and H. The annular space between A and B is suitably packed with leather, cotton waste, or asbestos, to prevent leakage between the upper and lower portions of A. As B and C are raised the valve F closes automatically, while H opens to admit the gas through D until the highest point of the stroke is reached. The gas originally present has meanwhile been

expelled through E. On the down stroke H closes and F opens, so that no transference of the gas as a whole takes place. The cycle is then repeated. Fig. 1 (VII) (b) shows a slightly different arrangement which has the advantage that no valves are needed on the piston.

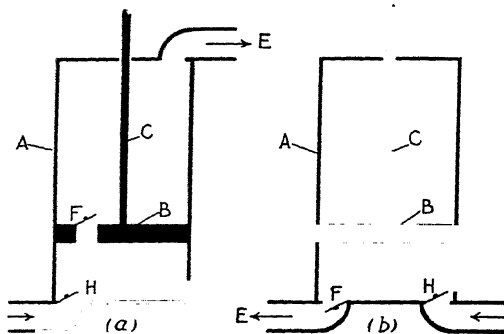


FIG. 1 (VII)

To obtain a more regular action two pumps may be arranged in parallel so that one piston is on the down stroke while the other is on the up stroke.

**The Water Jet Pump** is shown in Fig. 2 (VII) (a), (b), and (c). A is attached to a water tap. The jet issuing from B imprisons small bubbles of gas which are carried away through C and D, thus causing a continuous

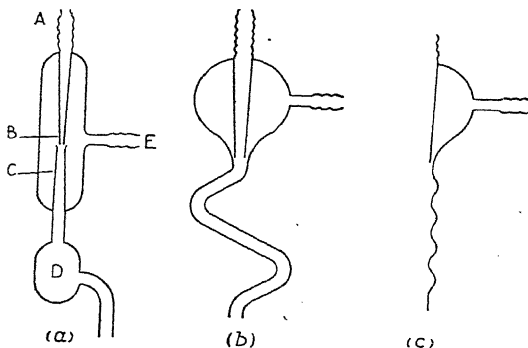


FIG. 2 (VII)

suction at E. In place of D, a zigzag tube or a series of constrictions may be used, or C may dip directly into a vessel of water.

This type of pump is very convenient for such operations as filtration under pressure, or vacuum distillation. The lowest pressure attainable is

usually considered to be limited by the vapour pressure of water, i.e. 5 to 15 mm. of mercury at the ordinary temperatures, but in actual practice this limit is sometimes passed by careful adjustment of the relative positions of B and C.

The principles related to jet pumps design and efficiency have been studied by Harrington.<sup>1</sup>

A complete circulation of gas can be obtained by some such apparatus as that shown in Fig. 3 (VII).

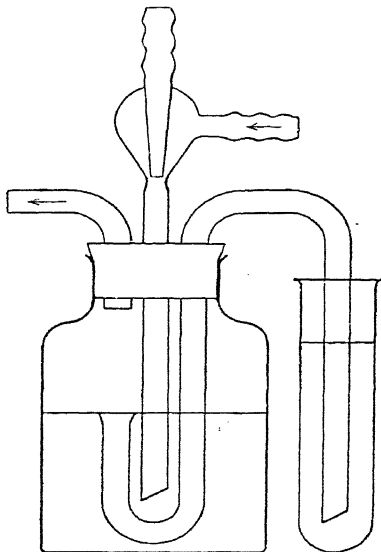


FIG. 3 (VII)

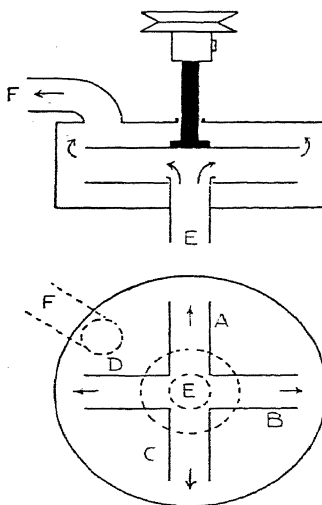


FIG. 4 (VII)

**The Centrifugal Pump.** Fig. 4 (VII) shows one form of centrifugal pump in plan and elevation. The four tubes A, B, C and D are rapidly rotated by means of a small motor, causing the gas to be sucked in at E, and expelled at F. Luther<sup>2</sup> has described a form of centrifugal pump capable of running at 3,000 r.p.m.

**The Fan Pump** is shown in Fig. 5 (VII). The fan ABC is rotated inside the case DEF, the gas being drawn in at H and expelled at K, or vice versa according to the sense in which the fan is rotated. A screw can, of course, be used in place of the fan.

**The Worm Pump.** An ingenious type of pump described by Wartenberg is shown in Fig. 6 (VII). A worm AB of two or three turns is rotated by means of the pulley C, inside the cylindrical chamber DE. A smaller chamber FH communicates with DE by the opening K. Both chambers

<sup>1</sup> *Rev. Sci. Inst.*, 1927, 14, 87.

<sup>2</sup> *Chem. Zeit.*, 1908, 32, 267.

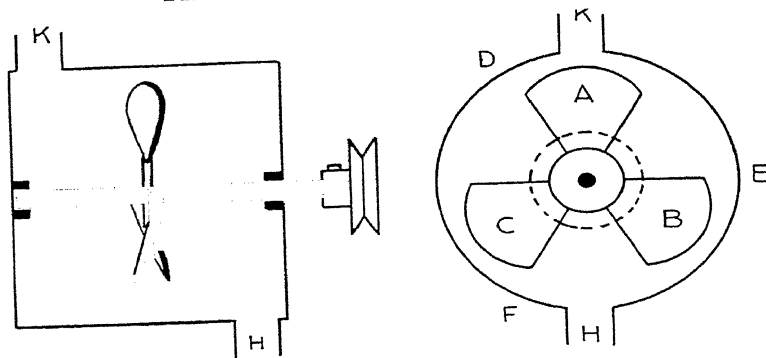


FIG. 5 (VII)

are filled with mercury to the level LM. Gas entering at P is entrapped by the worm at each revolution, carried to the opening R, and eventually discharged at Q.

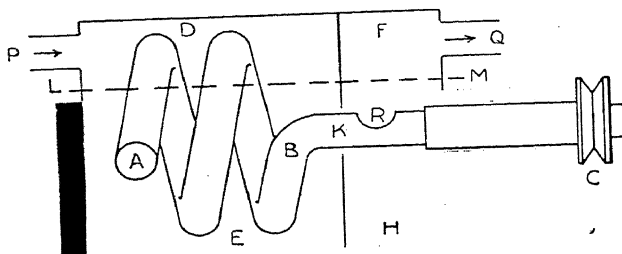


FIG. 6 (VII)

### The Rotary Piston Pump.

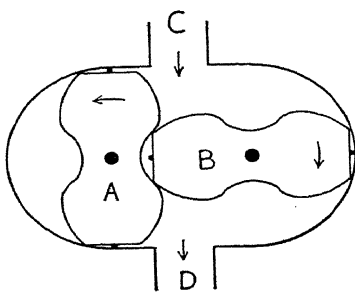


FIG. 7 (VII)

This type of pump (shown in Fig. 7 (VII)) is commonly known as 'Root's blower' or Connorsville pump. The two moving parts A and B rotate in a close-fitting casing at the same speed, but in opposite directions. Their form is such that A is always in contact with B at some point, a wide variety of such forms being possible. With rotation in the sense shown by the arrows the gas is continuously drawn in at C and expelled at D.

In the commoner varieties of the pump leakage at the points of contact becomes excessive when the difference of pressure between C and D reaches about 165 mm.

of mercury. This drawback can be overcome by using two or more pumps

connected in series when a greater difference of pressure is necessary. The pump is useful for propelling large quantities of gas against a small pressure head.

### COMPRESSION PUMPS

The operations in which the physical chemist is interested rarely require more than the compression of a definite mass of gas. It is then most convenient to produce a high pressure by some method which does not involve the use of a pump. As an example, Faraday's experiments on the liquefaction of gases may be quoted.

Where the continuous production of gas at a high pressure is desired, as for instance when making liquid air, a pump is necessary. At present one form or other of the piston pump is invariably used for such work. According to the final pressure required it is usual to effect the compression in two or more stages, the gas being cooled after each stage.

### EXHAUST PUMPS

The production of high vacua, on account of its technical and academic importance, has in recent years been the subject of much research, and the degree of vacuum obtainable is now limited only by the difficulty of entirely removing gases occluded in the walls of the vessel to be exhausted.

For practical purposes it is convenient to classify vacuum pumps according to the degree of vacuum attainable with each. This classification is roughly adhered to in the present section, but it must be borne in mind that in many cases individual pumps of the same type differ widely in their characteristics, and that the limiting vacuum obtainable depends not only on the pump but also on the way it is used.

The most important characteristics of a vacuum pump are (a) the initial pressure from which the pump functions, also termed the exhaust or 'rough' pressure; (b) the limiting pressure attainable on the 'fine' or low-pressure side; and (c) the rate at which the exhaustion takes place.

**Exhaust Pressure.** Except in the case of the Gaede and Holweck Molecular pumps the actual difference in pressure between the 'rough' and 'fine' sides is sensibly constant for a given pump, and hence the limiting pressure attainable is dependent on the 'rough' pressure. Most high vacuum pumps will not function unless the 'rough' pressure is below a certain limit. It is therefore usually necessary to connect a preparatory or 'fore' pump in series with the fine pump, to reduce the exhaust backing pressure of the latter to a convenient level.

**Limiting Pressure.** As stated above, the limiting pressure attainable with a pump depends largely on the exhaust pressure against which it works. This is usually due to leakage through the pump. There is theoretically no lower limit to the pressure attainable with mercury vapour pumps. With the molecular type the limiting pressure bears a constant *ratio* to the exhaust pressure.

**Speed.** The speed, *S*, of a vacuum pump at a given pressure may be



defined as the volume of gas at that particular pressure which the pump can remove per second. The speed may be measured at constant volume or constant pressure. For the former

$$S = \frac{v}{t} \log \frac{p_1 - p_0}{p_2 - p_0}$$

$v$  is the constant volume of the system being evacuated,  $t$  is the time in which the pressure falls from  $p_1$  to  $p_2$ , and  $p_0$  is the limiting pressure of the pump. In the constant-pressure method the volume of gas per second is measured which must be supplied to an enclosure being evacuated to keep the pressure constant.

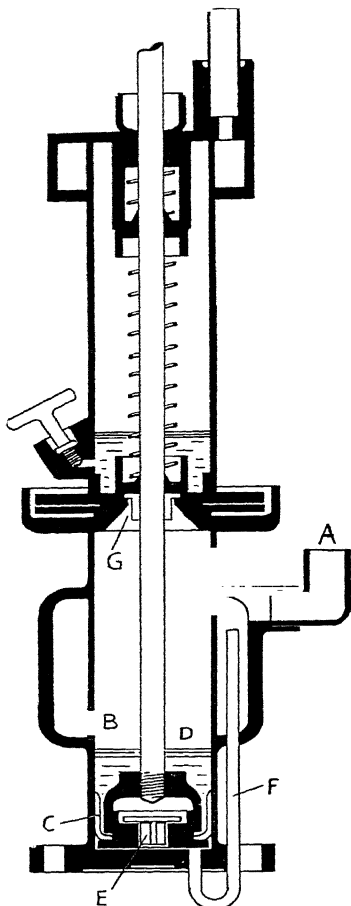


FIG. 8 (VII)

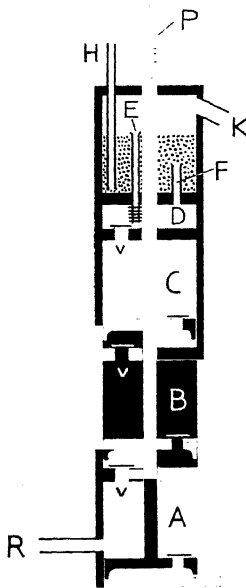


FIG. 9 (VII)

**The Geryk Pump.** This is shown in Fig. 8 (VII). The vessel to be exhausted is connected with A. The bucket leather of the piston C is pressed close to the cylinder wall by the oil in the space D. As the piston is raised from the position shown, the port B is cut off and the cylinderful of gas is forced through the valve G. The oil on the piston then mingles with the oil above G, the proper quantity being automatically returned as the piston descends. During the down-stroke the gas previously drawn in through B and F on the up-stroke is forced through the piston valve E.

A single-cylinder Geryk pump gives a limiting pressure of about 0.25 mm. of mercury.

**The Gaede Piston Pump** (Fig. 9 (VII) ) consists essentially of three pumps in series. Three pistons attached to the common piston rod P move in the chambers, A, B, and C, which communicate by the valves V. The gas is drawn from R, through A, B, and C successively, and forced through a layer of oil in the chamber D. The oil emulsifies with any water vapour present, and the emulsion is passed through the tube E on to a layer of fibrous material filling the top chamber. In percolating downwards the oil and water are separated, the oil remaining uppermost, and the water sinking to the bottom where it may be drawn off as often as necessary through the tube H. The oil overflows through F back into the chamber D, and the gas escapes at K.

According to Gaede a pressure of 0.00005 mm. of mercury (0.067 bar) can be obtained with this pump when exhausting into atmospheric pressure.

**The Cog-wheel Pump.** The pump shown in plan and elevation at Fig. 10 (VII) is a development of the rotary piston pump. The vessel to be exhausted is connected at A, and the gas expelled through the vent B. The whole apparatus is immersed in an oil bath which keeps it gas-tight and lubricates the moving parts. The cog-wheels must be adjusted carefully to prevent overheating, the normal speed being 800 to 900 r.p.m. A pressure of about 0.1 mm. of mercury can readily be obtained with this pump when new, but the limiting pressure gradually rises to 5 or 6 mm. of mercury after 1,000 hours use, or when the pump becomes overheated.

**The Gaede Rotary Oil Pump.** This pump was originally designed to act as a fore pump to the rotary mercury pump described on page 249, Fig. 18 (VII). One form is shown in Fig. 11 (VII) (a) and (b). A steel cylinder A rotates inside the steel casing G, the blades S being pressed into close contact with the walls by means of a spring. As the cylinder rotates, the gas is sucked in through C, forced through the valve D into the oil chamber O, and eventually expelled through J. The oil serves to render the apparatus gas-tight and also to effect lubrication of the moving parts. The shaft carrying the cylinder A is lubricated by a loose ring dipping into the oil in O. The entire apparatus is frequently immersed in an oil-bath.

Running at 400–500 r.p.m. against atmospheric pressure, a pressure of 0.01 to 0.02 mm. of mercury can be obtained with a single pump of this type in good condition. With two pumps in series a lower pressure is possible. Many types of the Gaede or 'Box' pump are now made. Unless an automatic stop valve is provided, care should be taken to prevent oil rising into the vacuum line.

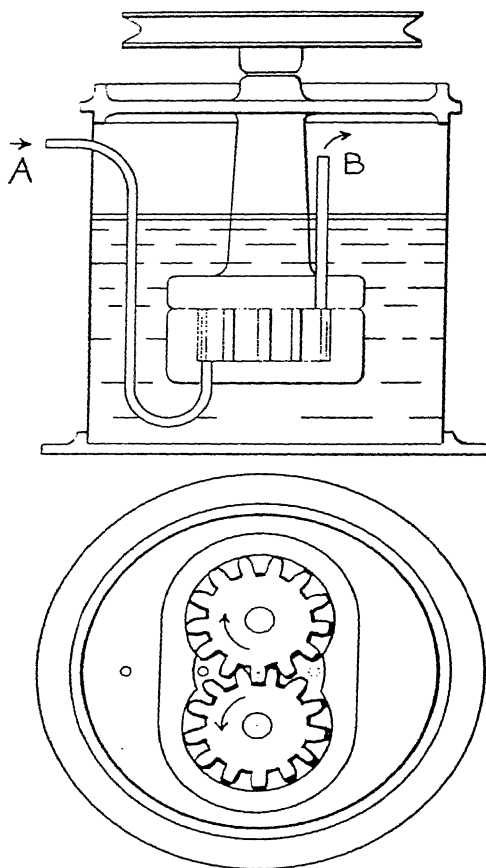


FIG. 10 (VII)

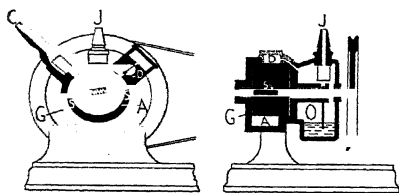


FIG. 11 (VII)

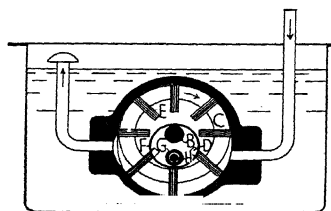


FIG. 12 (VII)

**The Trimount Pump** shown in Fig. 12 (VII) was designed to reduce leakage between the blades and casing. Eight blades are shown in the figure, but more or less may be used. Mechanical difficulties render regulation by springs undesirable. The method adopted is briefly as follows: The hollow cylinder C is fixed to and rotates about the axle B. The blades E move tightly in the slots D, each blade being composed of several independent leaves of steel. The cylindrical ring F is held in contact with B by the rowel G which rotates freely on the axis H. As C rotates, the blades are forced into close contact with the lower portion of the casing.

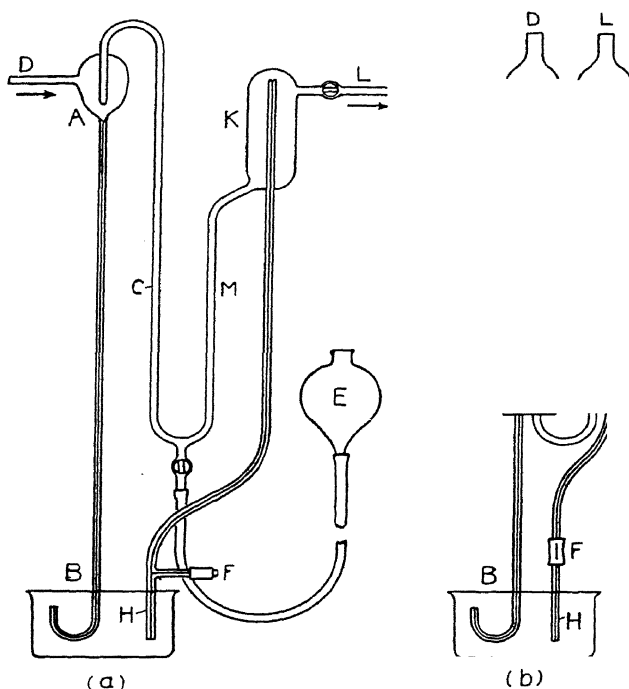


FIG. 13 (VII)

**The Sprengel Pump** bears a superficial resemblance to the common water-jet pump. One form is shown in Fig. 13 (VII) (a). AB is capillary tube of length about 125 cm. and internal diameter 1 to 2 mm. E is a mercury reservoir connected with C by a flexible tube. The vessel to be exhausted is connected at D. Disregarding the rest of the apparatus for the moment, it is evident that by raising E a jet of mercury will be caused to flow into the bulb at A. This jet breaks into small drops, imprisoning bubbles of the gas in A and carrying them away to be expelled at B. To obviate the necessity for replenishing E by hand a water-jet pump is connected to L,

by means of which mercury is drawn up through the capillary tube HK. F is an air inlet which serves to break the ascending mercury into drops enabling it to be raised to the reservoir at K. The air thus introduced is drawn off through L. K communicates with A by means of the tubes M and C, and a constant circulation of mercury results.

Fig. 13 (VII) (b) shows a modified form of Sprengel pump which can be constructed with very little difficulty. Its action will be evident from the foregoing description.

It is possible with the Sprengel pump to obtain pressures down to about 0.0007 mm. of mercury, this being the vapour pressure of mercury itself at ordinary temperatures, but to obtain such a pressure the internal diameter of AB must be small, as the mercury will otherwise fail to form air pockets. A fine capillary naturally reduces the speed of the pump, so that the two characteristics are, to a certain extent, opposed to one another. The speed varies between about 0.5 and 5 ml. per second.

Fig. 14 (VII) shows in outline a drawing of a double Sprengel pump used by Reilly and Pyne<sup>1</sup> in the vacuum distillation of certain organic substances. The substance was placed in the small flask. The first receiver was kept at a temperature of 50° to retain liquid products and the second receiver was surrounded by a freezing mixture. The gases given off during the reaction could be collected in the tube at the bottom. This apparatus was made by the Manchester Scientific Glass Co.

**The Cenco Pumps.** Instead of placing the blade or vane on the rotating member as in the types of pumps described above, it may be disposed in the casing. This construction is adopted for the 'Cenco' pumps made by Messrs. Central Scientific Co. of Chicago, U.S.A. The inlet and outlet ports are adjacent to each other and are separated by a vane passing through the casing which is under tension from a spring. The construction is shown in Fig. 15 (VII), which also illustrates the working of the pump—the rotating cylinder being shown in different positions. The entire pump is immersed in oil. In practice, two of the above units are mounted side by

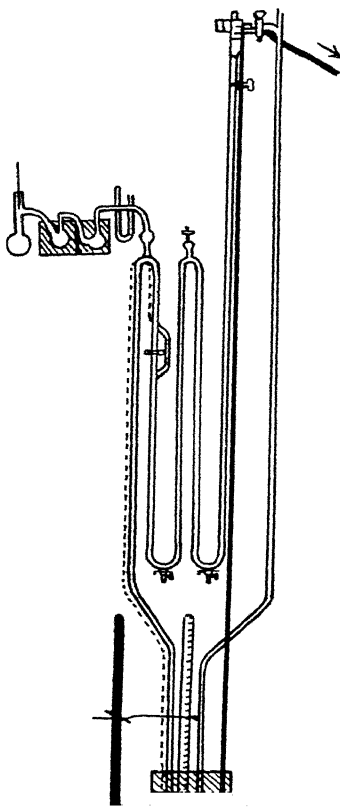


FIG. 14 (VII)

<sup>1</sup> *Sci. Proc. Roy. Dub. Soc.*, 1926, XVIII, 27, 329.

side on a common shaft, one acting as a backing (or fore) pump to the other. This is illustrated in Fig. 16 (VII), which shows the 'Hyvac' and 'Megavac' pump in phantom view. The vacuum claimed for the 'Cenco-Hyvac' pump is 0.3 micron (0.0003 mm.), while for the 'Cenco-Megavac' pump, the capacity of which is 3.25 times that of the 'Hyvac' model, the vacuum guaranteed is 0.1 micron or 0.0001 mm. of mercury. It is claimed that (with a liquid air trap) the latter type of pump finds many applications even where a diffusion or condensation pump is more usual. They may be used as a backing or fore-pump to all types of mercury pumps. In the 'Cenco-Hypervac 20' pump the reciprocating vane is made to operate two piston pumps. The construction of this vacuum pump is illustrated in Fig. 17 (VII). The rotating cylinder A is seen with the vane C standing on it. When air is drawn in through the inlet pipe D it is compressed by the rotor and discharged through the ball-valve B into the cylinder F, in which a piston G is actuated. On the completion of the compression movement of the rotor the piston G is at its highest

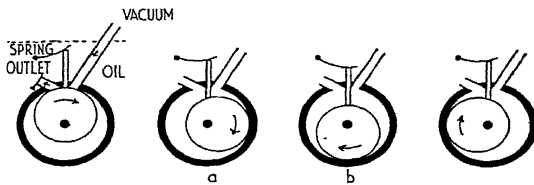


FIG. 15 (VII)

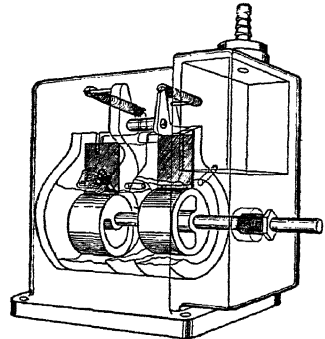


FIG. 16 (VII)

position in the cylinder, and on the further rotation of A the piston descends, transferring through its two ball valves the air from its underside. This air is finally discharged to the atmosphere on the second upward stroke of the piston. The projection on the piston operates the upper valves, which also admit a quantity of oil. The piston and cylinder E on the other side of the vane acts as a rough pump and also removes gases and volatile material from the oil before it passes to the bearings. The 'Hypervac' pump is claimed to produce a vacuum of 0.00005 mm., while a vacuum of 0.0001 is guaranteed. In the 'Cenco-Hypervac 100' pump the 'roughing' or fore-pump is a complete 'Cenco-Hyvac' unit built into the housing. Means are provided for by-passing automatically this unit when large volumes of gas are being handled. Means are provided to have all the oil except that sealing the exhaust ports maintained under a pressure of a few microns. This includes the lubricating oil in the bearings, the oil which seals all the high-vacuum spaces against atmospheric pressure as well as the oil which enters the finishing or fine stage for lubrication purpose. The pump is of value where large volumes are required to be exhausted rapidly to low pressures. The vacuum guaranteed is 0.0001 mm., while exhaustion to 0.00002 mm. is also claimed. The following table reproduces data for these pumps supplied by Messrs. Central Scientific Co., Chicago.

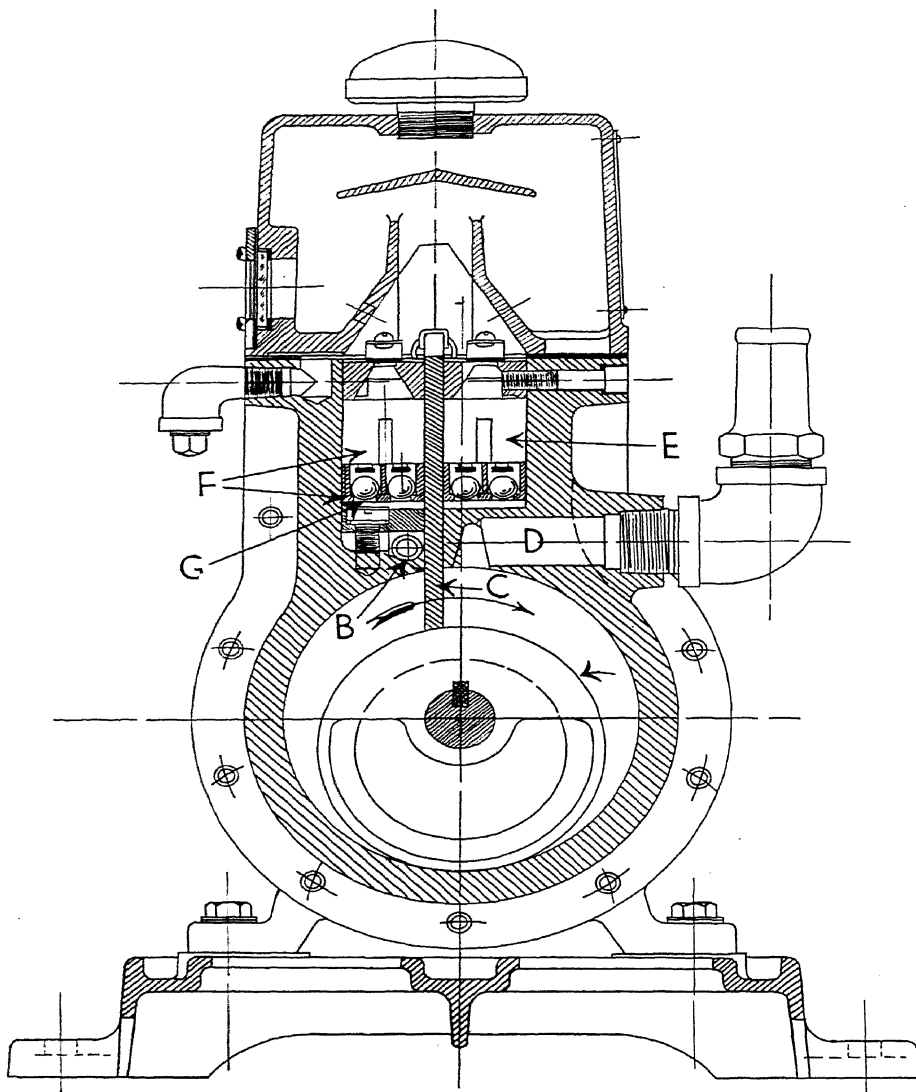


FIG. 17 (VII)

	Hyvac	Megavac		Hyper- vac 20	Hyper- vac 100
		Size 1	Size 2		
Guaranteed vacuum, microns ( $\mu$ ) .	0.3	0.1	0.1	0.1	0.1
Pump speed, r.p.m. . . . .	350	325	600	425	450
Capacity, free air, ml./sec. . . .	170	510	940	3,300	16,000
Capacity, free air, litres/min. . .	10	31	57	198	960
Pumping factor <sup>1</sup> . . . . .	1	3		20	100
Size of motor, h.p. . . . .	$\frac{1}{8}$		$\frac{1}{2}$		$1\frac{1}{2}$
Diameter of pump intake, inches			$\frac{5}{8}$	13/16	3.5 <sup>2</sup>
Minimum starting temp., degrees .	15	15	15	15	15

<sup>1</sup> Ratio of speed to that of Hyvac under same conditions.

<sup>2</sup> Threaded for standard 3-inch pipe.

**Gaede Rotary Mercury Pump.** Fig. 18 (VII) (a) and (b) shows the essential parts of this pump. The porcelain drum H rotates on the axis K

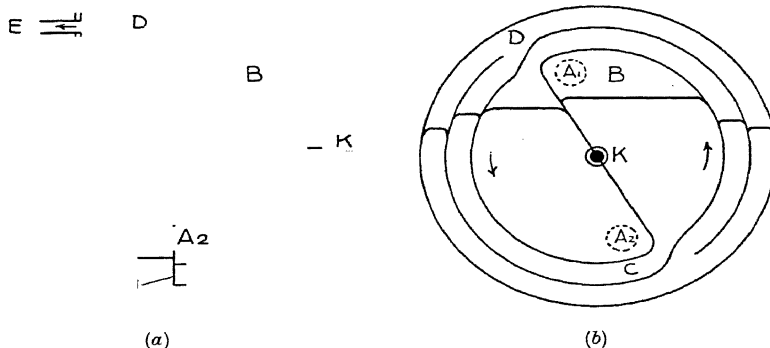


FIG. 18 (VII)

inside the iron casing which is provided with a stout glass window G. The vessel to be exhausted is connected at R, and a rough 'fore pump', giving 10 to 15 mm. of mercury pressure, is connected at E. As H rotates in the direction shown by the arrows the space B continuously increases in volume, causing the gas to be sucked through the port  $A_1$  from R.  $A_1$  is then closed by the mercury during the second portion of the revolution, as shown at  $A_2$ , and the gas in B is forced through C into the space D, from whence it is extracted through E by the fore pump. The other half of the drum is meanwhile performing a similar cycle of operations.

The degree of vacuum obtainable with this pump is in the neighbourhood of 0.1 bar (0.00007 mm. of mercury). The maximum speed of exhaust is about 100 ml. per second.

**The Toepler Pump.** In this type of pump (Fig. 19 (VII) ) mercury



is used as the piston. No valves are required except a rough glass valve G, which prevents the mercury entering the vessel to be exhausted, E. The pump is operated by alternately raising and lowering the mercury reservoir

R. At each upward stroke the gas in B is forced through the tube F, and the mercury seal at M, into the atmosphere. On the downward stroke the gas in E is enabled to expand into B. The tube below B must obviously be of barometric length.

Pressures as low as 0.01 bar (0.000007 mm. of mercury) have been attained with the Toepler pump, but it has the disadvantage of requiring personal attention. The speed of exhaust is low—about 0.35 ml. per second.

**Molecular Pumps.** The principle of the molecular pump is illustrated at Fig. 20 (VII). A cylinder A is caused to rotate at a high speed in a close-fitting casing B. A slot is cut from C to D, each end of which is connected

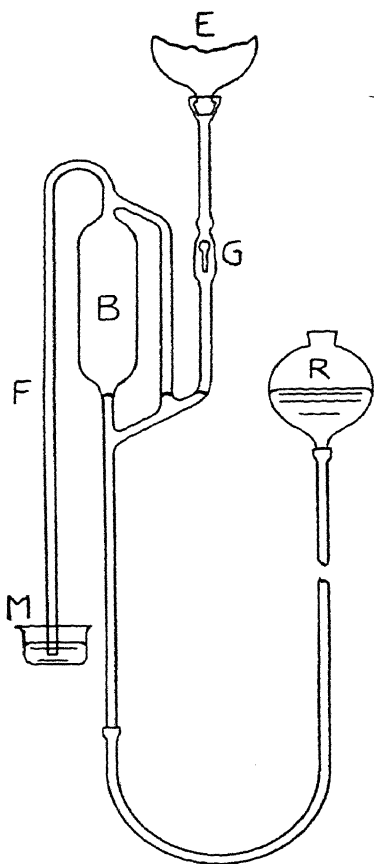


FIG. 19 (VII)

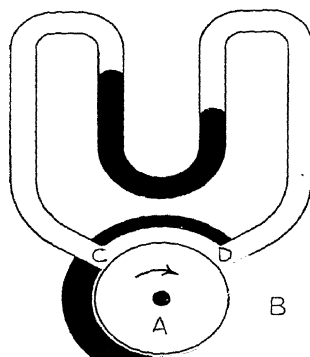


FIG. 20 (VII)

to a manometer. Due to the rotation of A a pressure difference is set up between C and D. Provided the initial pressure is low enough, it has been shown that  $\frac{P_1}{P_2} = Ku$ , where  $P_1$  and  $P_2$  are the pressures at C and D, K is a constant depending on the dimensions of the slot CD and the nature of the gas, and  $u$  the speed of rotation of A.

In applying this principle to the construction of vacuum pumps it is usual to make CD as long as possible, and to rotate A at a very high speed.

**The Gaede Molecular Pump.** As shown in Fig. 21 (VII) (a) and (b), the rotating cylinder carries a number of parallel slots which receive projections from the outer casing. These slots communicate with one another

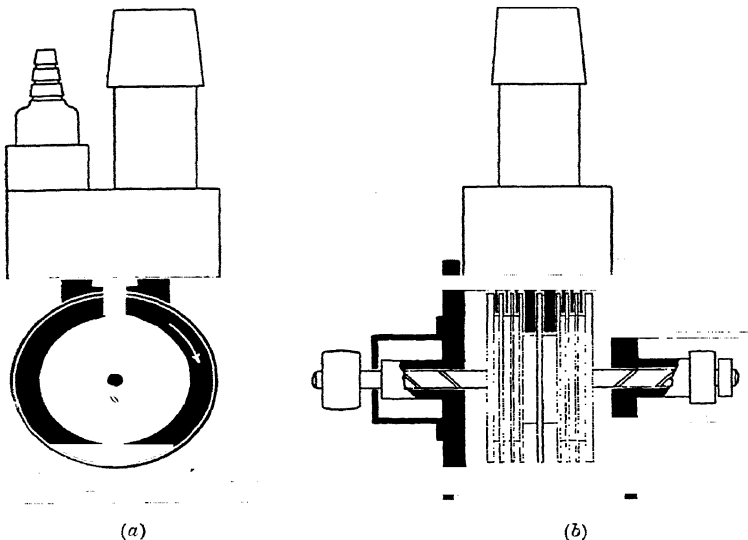


FIG. 21 (VII)

in series in such a way that the pressure is lowest in the outermost ones. The fore pump tends to draw oil from the bearings to the interior, and since this would be detrimental to the action of the pump, the shaft is slotted to force the oil outwards by centrifugal action. It is, therefore, important to have the molecular pump running before the preparatory pump is started. At 8,000 r.p.m. the ratio of the fore to the exhaust pressure is about 1 : 50,000. This ratio, of course, controls the limiting pressure for a given fore pump. The speed of exhaust depends on the exhaust pressure. A more recent type of this pump was the 'Cenco-Aristovac'<sup>1</sup> pump, but this design has now been discontinued by the makers.

**The Holweck Molecular Pump** is shown in Fig. 22 (VII). The rotor F is a plain cylinder. The outer case has two helical slots G which originate at M and end at N, the depth gradually decreasing from M to N. The fore pump is connected at B, which communicates with the end space O through the channel P. The vessel to be exhausted is connected to A, which communicates with L.

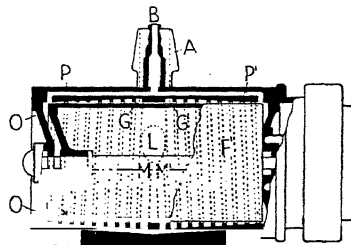


FIG. 22 (VII)

<sup>1</sup> Messrs. Central Scientific Co., Chicago.

A totally enclosed electric motor rotates F normally at 4,000 r.p.m. The ratio of the fine to exhaust pressure varies from 1 : 100,000 to 1 : 70,000,000. A limiting pressure of 0.000001 mm. of mercury (0.0013 bar) is claimed to have been obtained with an exhaust pressure of 70 mm. of mercury, and it is stated that the exhaust pressure may be as high as 90 mm. of mercury without seriously affecting the efficiency. The speed of exhaust is in the neighbourhood of 2,300 ml. per second.

**The Gaede Diffusion Pump.** The vessel to be exhausted is connected at F (Fig. 23 (VII) ). This is an early model of the pump. L and M communicate with the fore pump; the former connection, being used merely to hasten the first stages of the exhaust, is cut off automatically by the manometer when the pressure becomes low enough for the diffusion pump to act. The mercury at A is heated, and the vapour, rising first through the annular space B, is constrained to pass through D and E to the condenser K. The condensed mercury then falls back to replenish A. The steel cylinder C carries a slit S, whose width can be adjusted by the screws H. G is a mercury seal which separates the high- and low-pressure portions of the pump. Gas in the neighbourhood of S diffuses into the mercury vapour stream and is carried away by it and extracted at M. Any mercury vapour passing out through S is condensed by the condenser P. T is a thermometer which registers the temperature of the vapour.

According to Gaede's theory the speed of exhaust is at a maximum when the width of the slit S is of the same order of magnitude as the mean free path of the gas molecules in the slit, and the mercury vapour pressure slightly greater than the pressure given by the fore pump. In practice, to obtain the maximum speed (with a given fore pump and size of slit) requires a fairly critical adjustment of the vapour pressure, and consequently of the temperature as shown by T. The speed does not alter appreciably at low pressures.

In the Gaede diffusion pump the stream of mercury vapour in flowing past the orifice or slit carries with it the air or gas molecules which diffuse through the slit, but mercury vapour also diffuses back through the slit. This is, however, condensed. In the Langmuir condensation pump the mercury vapour is prevented from diffusing back through the aperture leading to the system being evacuated by condensing the vapour around the aperture. The size of the orifice does not then become so critical, but by the use of a directive aperture (e.g. in the shape of an annular jet) more efficient entraining of the air molecules may be secured.

**The Condensation Pump.** Fig. 23a (VII) shows one form of the condensation pump, invented by Langmuir. The mercury in the bulb A is vaporized by some form of heater. The vapour passes through the curved neck B and escapes from the orifice C. Gas from the vessel to be exhausted passes from R through the mercury-vapour trap D (which is cooled in liquid air when very low pressures are required), and diffuses into the blast of mercury vapour issuing from C. The mercury vapour is condensed almost immediately by the condenser E, but the gas molecules acquire a velocity sufficient to carry them from C to be extracted through F by the fore pump. The condensed mercury returns to A by way of the tube H. It is important to note that the overflow tube of the condenser E is somewhat higher than the orifice C as shown in the figure. C may be enlarged to any reasonable

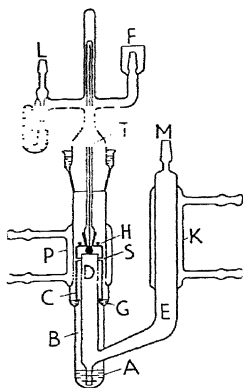


FIG. 23 (VII)

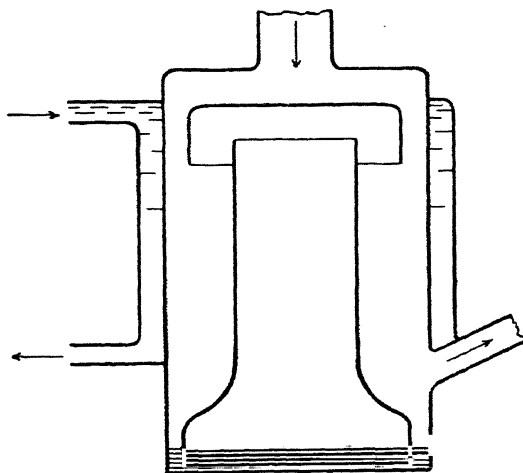


FIG. 24 (VII)

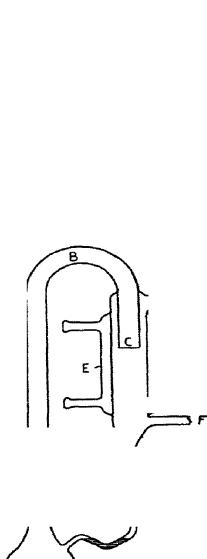


FIG. 23a (VII)

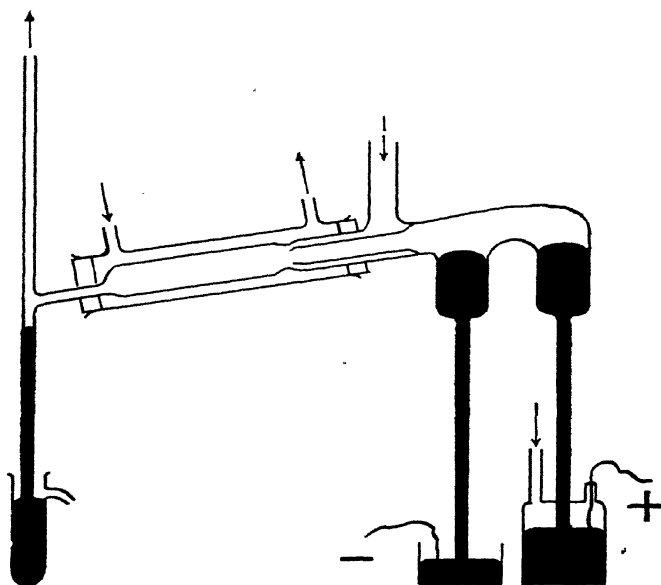


FIG. 25 (VII)

diameter provided the mode of heating adopted is adequate; the speed of exhaust increases proportionately. There is nothing critical about the adjustment of the temperature of the vapour, as is shown by the fact that when using an electric heater, the current consumption may be varied through a wide range without affecting the operation of the pump.

Various forms of the condensation pump have been described from time to time. It may easily be constructed by anyone possessing a knowledge of glass-blowing, and the constructor may adopt any design which suits his needs since the dimensions are not critical. Fig. 24 (VII) shows a pump

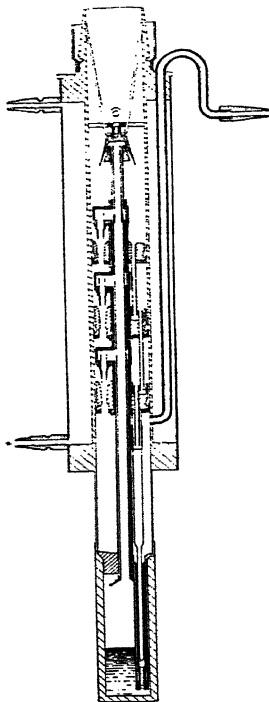


FIG. 26 (VII)

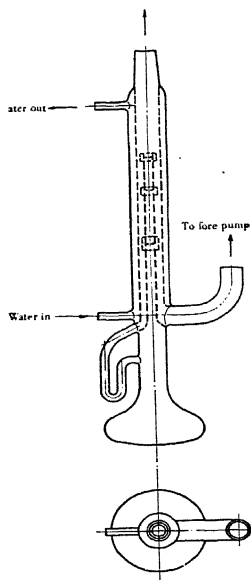


FIG. 27 (VII)

made entirely of metal, and Fig. 25 (VII) one where the mercury is vaporized by an electric arc. This latter acts as a mercury still. On account of its heat-resisting properties, fused quartz is commonly employed. All-metal construction is frequently used.

A condensation pump with one diffusion aperture would require a backing (or fore) vacuum of approximately 0.1 mm., but multi-stage pumps having two or more jets each acting as a backing pump for the former stage will operate with a backing vacuum to the whole pump of as high as 20–40 mm. mercury in the case of a four-stage pump. Fig. 26 (VII) shows the four-stage pump of Firma E. Leybold's Nachfolger. In Fig. 27 (VII) the three-stage

pump of Messrs. The Thermal Syndicate, Ltd., Wallsend-on-Tyne, is illustrated. It is stated that the maximum fore pressure with which the pump will operate satisfactory is 8.5 mm. and the vacuum attainable is 0.000009 mm. of mercury pressure. The speed of the pump varies with the fore pressure used and is calculated from the usual expression

$$S = \frac{V}{t} \log_e \frac{(P_1 - P_0)}{(P_2 - P_0)}$$

where  $S$  = speed in ml. per minute

$t$  = time in minutes for the pressure to fall from  $P_1$  to  $P_2$  mm. of mercury

$P_0$  = minimum pressure in mm. of mercury attainable

$V$  = volume in ml. of system evacuated

The makers give the following figures for the performance of the pump :

Fore pressure mm. of mercury	Mean speed (ml./min.) to attain a vacuum of 0.000009 mm. mercury
8.5	100
6.2	400
0.0044	2,470

A description of the electrically heated all-metal Gaede-Volmer Mercury Condensation pumps as made by Firma E. Leybold's Nachfolger may be given. The pumps consist of (a) the 'pump body' and (b) the 'interior fittings', which may be withdrawn from the pump body for cleaning and control (see Fig. 28 (VII)).

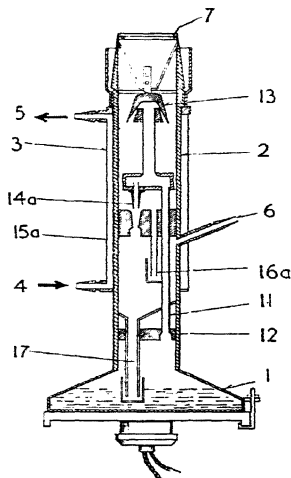


FIG. 28 (VII)

The pump casing consists of the flat mercury boiler (1) serving to hold the mercury for operating the pump, and the pump jacket (2) which carries the cooling jacket (3), with the water supply and water outlet pipes (4) and (5). The backing vacuum tube (6) passes through the cooling jacket. The upper end of the pump jacket forms a ground joint and serves to connect with the high vacuum receiver. A metal ring (7) which is inserted into the high vacuum nozzle of the pump prevents any grease that may be forced out from the joint from dropping into the pump.

The removable interior fittings are carried by the vapour tube (11). At (12) the boiler is hermetically sealed from the pumping chamber proper. The vapour rising in (11) reaches the diffusion nozzle (13) and the jet nozzle (14a).

Other types of pumps are provided with a further one or two jet nozzles which are arranged in a similar manner. Each jet stage operates as a backing pump for the preceding stage and the sections operating at different pressures are separated by partitions (15a).

The mercury condensed in the different stages flows through the overflow tubes (16a) to the tube (17) and then returns to the boiler.

Mercury-vapour pumps will not reduce the pressure in an evacuated

apparatus below the vapour pressure of the mercury in the system (approximately 0.001 mm. at ordinary temperatures). The mercury vapour may, however, be condensed by a liquid-air trap inserted between the pump and the apparatus. Liquid air ( $-183^{\circ}$ ) will, of course, also liquefy any other condensable vapours in the system. In addition, charcoal in a container cooled in liquid air will adsorb considerable quantities (up to one thousand times its own volume) of gases or vapours. Mercury vapour may also be trapped by use of an alkali metal surface.

Charcoal was first suggested for the trapping of oil vapour by Becker and Jaycox.<sup>1</sup> In the common type of charcoal traps used in oil-vapour pumping systems the charcoal is 'outgassed' at temperatures of the order of  $500^{\circ}$  by wire-wound resistance heaters enclosing a glass containing tube and the final vacuum obtained by cooling the charcoal to laboratory temperature. As pointed out by Anderson,<sup>2</sup> this involves a prolonged baking period (24 hours or more) owing to the sluggishness of 'outgassing'. He has designed a trap of low kinetic resistance requiring very little preliminary heating (*l.c.*) and the author should be consulted for details.

Liquids other than mercury have been proposed for use in condensation pumps, e.g. high boiling point esters and petroleum products. Among esters which have been utilized in condensation pumps are (i) *n*-dibutyl phthalate, (ii) 2-ethyl-hexyl-phthalate (octoil) and (iii) 2-ethyl-hexyl-sebacate (octoil-s). The last two liquids have the following characteristics:

	Approximate vapour pressure $25^{\circ}$	Best vacuum with cooling water at $15^{\circ}$	
		Single boiler pump	Multi-boiler pump
2-ethyl-hexyl-phthalate . . . .	$5 \times 10^{-7}$	$10^{-5}$ mm.	$6 \times 10^{-7}$ mm. <sup>1</sup>
2-ethyl-hexyl-sebacate . . . .	$5 \times 10^{-8}$	$10^{-5}$ mm.	$3 \times 10^{-8}$ mm. <sup>1</sup>

<sup>1</sup> Measurement with ionization gauge in Kodak Research Laboratories. The Eastman Kodak Co., Rochester, N.Y., can supply both these chemicals.

A range of high-vacuum pumping equipment ('Metrovick') using condensation pumps in which 'Apiezon' oil products<sup>3</sup> are the working fluids are now available.<sup>4</sup> These oils are obtained by the evaporative distillation of petroleum products (cf. Burch, *Proc. Roy. Soc.*, 1929, A, 123, 271, and British Patent No. 346,293 (1931)). They have remarkably low vapour pressures ( $10^{-5}$ – $10^{-7}$  mm. at room temperatures) and when used in condensation pumps the necessity for a trap no longer exists. Two types of 'Metrovick' oil condensation pumps are made for general purposes, viz. types 02 and 03. The former is designed for operation with a high backing (or fore) pressure and the latter to have a high pumping speed as well as a high ultimate

<sup>1</sup> *Rev. Sci. Inst.*, 1931, 2, 773.

<sup>2</sup> *Ibid.*, 1937, 8, 263 and 493.

<sup>3</sup> 'Apiezon' (from the Greek *ἀπειζόν* = without pressure) oils are obtainable from Technical Products, Ltd., London.

<sup>4</sup> Messrs. Metropolitan-Vickers Electrical Co. Ltd.

vacuum. In one 'Metrovick' set of pumping equipment one of each of the above types of oil condensation pumps is used in series with a rotary oil or 'box' pump which provides the backing (or fore) vacuum to the type 02 pump which in the set follows the type 03 model. The combination is also provided with a reservoir between the two oil condensation pumps to prevent sudden evolution of gas from reducing the speed of evacuation, i.e. reduction of the pressure. This would arise if the fore pressure to the first stage pump (Type 03) were to reach such a value that it could no longer function. The speed is then determined by the type 02 pump which has a speed of 4 litres per second in contrast with 20 litres per second of the type 03 pump (both for pressures below  $10^{-3}$  mm. on the fine side). It may be mentioned here that as the speed of a pump is defined as the volume of gas abstracted per second from the system being evacuated at the pressure produced by the pump, then the speed of a fore pump need be but a small fraction of that of a pump to which it is providing the fore vacuum. The 'Metrovick' equipment described above is of all-metal construction—this including the valves for isolating the evacuated system, &c. These are the Audco<sup>1</sup> Type FV High Vacuum Valves, which are claimed effectively to isolate vacua of  $10^{-5}$  mm.

The adoption of the reservoir is recommended only in cases where it is desirable to be able to shut down the pumping plant under a comparatively high vacuum, e.g. that produced by the 02 pump. In this case an Audco valve is inserted on the high-vacuum side of the 02 pump. The limiting speed of the Audco valve may, however, act as the limiting feature of the pumping plant as a whole, and in the event of a sudden evolution of gas of short duration the backing pressure of the 03 pump may rise above the pressure at which the pump ceases to operate. The reservoir would accommodate any such sudden evolution of gas and prevent any appreciable rise in pressure which might have unfortunate consequences, particularly in thermionic work. In cases where it is not necessary to shut down the apparatus under a high vacuum, but it is desired to maintain a high pumping speed, the reservoir may be omitted and the backing pipe from the 03 pump connected directly to the high-vacuum side of the 02 pump. Using this combination, the apparatus can be shut down under a vacuum equal to that produced by the rotary pump.

See later in this section for a detailed description of the type 03 pump.

The oil condensation pumps are usually heated electrically to prevent overheating and decomposition of the oil. It is also necessary to provide a drying trap to absorb water vapour between the fore vacuum pump and the oil condensation pump. Mercury vapour should also be absent from the system. Air should not be re-admitted to the pump while hot.

Apiezon oil products may also be used for luting purposes. The properties of these oils, greases and waxes are given in the table on next page and in the subsequent note.

**Apiezon Oil 'A'.** This is a special low vapour-pressure oil which is specially recommended for use in the type 02 oil condensation pump manu-

<sup>1</sup> Messrs. Audley Engineering Company.



factured by Messrs. Metropolitan-Vickers Electrical Co., Ltd.<sup>1</sup> It has a vapour pressure of the order of  $10^{-5}$  mm. of mercury at the usual cooling water temperature ( $15^{\circ}$  to  $20^{\circ}$ ). This is the limiting pressure to which it is possible to exhaust an ionization gauge on such a pump when using this oil without the use of artificial refrigerants.

Apiezon product	Application	Vapour pressure at room temperature after evolution of dissolved air	Safe maximum temperature in use	Temperature to which sealing media should be raised to apply
Oil 'A'	Condensation pumps	0.01 micron <sup>1</sup> at room temperature	—	—
Oil 'B'	Condensation pumps	0.0001 micron at room temperature	—	—
Oil 'J'	For oil lubricated taps and places where a moderately viscous oil of low vapour pressure is required	1 micron at $250^{\circ}$	—	—
Oil 'K'	For places where an exceedingly viscous oil of very low vapour pressure is required	1 micron at $300^{\circ}$	—	—
Grease 'L'	Ground well-fitting joints. Temporary work	1 micron at $300^{\circ}$	$30^{\circ}$	Room temp.
Grease 'M'	For places where a grease of moderately low vapour pressure is required	1 micron at $200^{\circ}$	$30^{\circ}$	Room temp.
Grease 'N'	Glass conical taps	1 micron at $200^{\circ}$	$30^{\circ}$	Room temp.
Sealing Compound 'Q'	Unground joints	0.1 micron at room temperature	$30^{\circ}$	Room temp.
Wax 'W'	Permanent joints	1 micron at $180^{\circ}$	$80^{\circ}$	$100^{\circ}$
Wax 'W40'	Semi-permanent joints at room temperature. Joints subject to vibration	1 micron at $180^{\circ}$	$30^{\circ}$	$40^{\circ}$ to $50^{\circ}$

<sup>1</sup> 1 micron =  $10^{-3}$  mm. mercury

**Apiezon Oil 'B'.** This is an oil of even lower vapour pressure than 'A' oil. It is recommended for use in the type O3 pump for general high vacuum purposes, for example, the exhaustion of thermionic valves.<sup>2</sup> The limiting pressure producible in this way without the aid of refrigerants (i.e. the vapour pressure of the oil at the temperature of the pump cooling water) has been found to be  $10^{-7}$  mm., the measurement being made by an ionization gauge, the calibration of which had been made with air.

**Apiezon Oil 'J'.** This is a dark oil having an olive-green bloom. It is primarily prepared for use in a special vacuum tap designed by the Audley Engineering Co. in conjunction with Messrs. Metropolitan-Vickers. The oil is, of course, required for the lubrication and sealing of the 'Audco' tap, as an ordinary lubricant would be useless where low pressures are concerned. Although it is definitely designed for the purpose mentioned, it can also

<sup>1</sup> In this modified O2 pump the following are the relative figures: Speed, 6 litres/sec, at pressures below  $10^{-2}$  mm. Hg. on the high vacuum side. Highest possible backing pressure is 0.3 mm.

<sup>2</sup> This pump is considered on p. 260.

be used as a sealing medium wherever such a viscous oil is found necessary.

This oil is manufactured by a distillation process prolonged until the vapour pressure, as deduced from the observed evaporating speed, estimated molecular weight, and known evaporating area of the still, has fallen to  $10^{-3}$  mm. at  $250^{\circ}$ .

**Apiezon Oil 'K'.** This oil is similar in appearance to the last mentioned oil, but has a much higher viscosity. This material is manufactured by a distillation process, prolonged until the vapour pressure (deduced in the manner described for 'J' Oil) has fallen to  $10^{-3}$  mm. at  $300^{\circ}$ .

**Apiezon Grease 'L'.** This is a special grease approximately of the consistency of 'vaseline' being designed for the sealing of ground-glass vacuum joints and for other similar purposes.

The material is manufactured by a distillation process, prolonged until the vapour pressure has fallen to  $10^{-3}$  mm. at  $300^{\circ}$ . Measurements of the vapour pressure by observation of evaporation rate have been attempted with the grease at  $70^{\circ}$  and the condensing surface cooled by liquid air. No trace of distillate could be detected. This is to be expected, since a vapour pressure of  $10^{-3}$  mm. at  $300^{\circ}$  would imply a vapour pressure of about  $10^{-11}$  mm. at room temperature.

**Apiezon Grease 'M'.** This material is manufactured by a distillation process, prolonged until the vapour pressure has fallen to  $10^{-3}$  mm. at  $200^{\circ}$ . This would imply a vapour pressure of the order of  $10^{-6}$  to  $10^{-7}$  mm. at room temperature. This grease is suited for use as a sealing medium on ground joints, &c., where the more expensive Apiezon Grease 'L' is not justified by an extremely low vapour pressure.

Experiments have shown that the grease has a vapour pressure of  $6.10^{-7}$  mm. at  $50^{\circ}$ .

**Apiezon Grease 'N'.** This is a rubber grease specially suitable for the lubrication and sealing of glass conical taps used in high vacuum apparatus. The vapour pressure is low enough at room temperature for the material to be suitable for use in thermionic experiments. It should not be used at temperatures exceeding  $35^{\circ}$ . The taps should be made lukewarm before assembling with this grease, but the latter may be applied at room temperature.

**Apiezon Sealing Compound 'Q'.** This product is firm at temperatures up to about  $30^{\circ}$ , but sufficiently soft to allow of easy moulding into position. It can be made to adhere to any reasonable surface to make a vacuum-tight seal. Sealing Compound 'Q' will not give off any appreciable quantity of gas when introduced to a vacuum as would an ordinary putty.

This material is of special utility for work where a vacuum-tight seal is required, but where the use of Apiezon Grease 'L' is prohibited by cost or because the joint is not sufficiently well flatted, as in testing operations where it is necessary to blank off temporarily a portion of the apparatus. In such a case the open end of the pipe has merely to be roughly stopped by a plug or just a piece of plate and then sealed with a little putty to give a leak-proof blank.

A material which will enable this to be done so simply and yet so efficiently with little time, trouble, or expense will prove invaluable wherever it is

required to make a temporary joint on vacuum systems without any elaborate or highly skilled process, such as grinding surfaces optically flat. The joint made by means of Apiezon Sealing Compound 'Q' is quickly assembled and dissembled and is absolutely reliable for temporary joints where grease would be useless.

Apiezon Sealing Compound 'Q' is intended for use in cases where Apiezon Grease 'L' is impracticable. It cannot replace the latter on vacuum systems, such as those employed in valve work, where an extremely high degree of evacuation has to be maintained.

**Apiezon Sealing Wax 'W'.** This is a black material having a softening point of 80°-90° and a vapour pressure sufficiently low to permit its use as a material for sealing joints in high vacuum systems. When it is heated in an evaporating still to 180°, distillation begins at a rate indicating a vapour pressure of about  $10^{-3}$  mm., which would imply a vapour pressure less than  $10^{-6}$  mm. at room temperature.

**Apiezon Sealing Wax 'W40'.** It has been found that wax 'W40' has several useful applications where ordinary Wax 'W', due to its brittleness, would be unsuitable. The former flows at a lower temperature than Wax 'W', having a melting-point of 40° compared with 100°. At room temperatures it is plastic and easily moulded by the fingers. Also it is less brittle than 'W' and is more suitable for sealing joints which remain at approximately room temperatures but which are subject to vibration under operating conditions. There is less likelihood of the wax cracking in such circumstances.

Further, this material is suitable for application in cases where it is required to flow the sealing material into or around the joint, but at the same time it is desirable to keep the temperature of the parts as low as possible. This might occur when using this material to seal a flat glass flange to a metal flange since there would be a greater danger of cracking the glass if higher temperatures were required in order to make the sealing medium flow freely.

It is not recommended due to its low melting-point that this product should be used to seal parts that become warm under operating conditions, e.g. up to temperatures of 35° or thereabouts as Wax 'W40' would tend to run from the joint. The Wax 'W' should be used in such instances.

**Description of Type 03 'Metrovac' Oil Condensation Pump.<sup>1</sup>** This pump (Fig. 29 (VII)) operates on the condensation principle and employs Apiezon low vapour-pressure oil as the working fluid. The body of the pump and the water-jacket are constructed from a non-corrodible alloy, while the oil reservoir below is made of copper to provide high heat conductivity.

For boiling the oil, the pump employs a specially designed electrical heating element having a long working life. This is fitted by means of a single bayonet clip and may thus be easily replaced. The heater can be wound for any one supply between 110 and 250 volts, and is provided with a standard plug.

Various forms of high vacuum connection can be supplied, depending on the service for which the pump is intended : (a) Accurately ground flat steel

<sup>1</sup> Made by Metropolitan-Vickers Electrical Co., Ltd., Manchester.

flange. (b) Glass-to-steel ground conical joint, including steel tube and two lengths of glass tube. (c) Connection for waxed joint incorporating annular water passage. (d) Plain solid drawn steel tube of any specified length for welding to customer's apparatus.

Rubber tubing water connections are fitted as standard, but fittings for metal tubing can be supplied if specified. The pump is arranged for rubber tube connection to the backing pump, but a special oil-sealed union for metal pipe connection to the backing pump can be supplied instead.

*Specification.* Type of oil, Apiezon 'B'; volume of oil, 75 ml.; limiting pressure,  $5 \times 10^{-6}$  mm. of mercury; speed, 20 litres/sec. at pressures below  $10^{-3}$  mm. of mercury on the high vacuum side; highest permissible backing pressure, 0.05 mm. of mercury; power consumption, 275 watts.

Before deciding the correct solution to any vacuum pumping problem, it is important to know all the details concerning the final vacuum and rate of evacuation required in addition to having a full knowledge of the performance of the pumps. Metropolitan-Vickers' Research Department has a very wide experience in the design and operation of high vacuum apparatus of many different kinds, and it is recommended that research workers should submit full details of their individual problems so that the pump supplied may be the most suitable for their requirements. These will depend on (1) supply voltage, (2) type of high vacuum connection, (3) type of connection to backing pump, (4) whether a pump stand fitted with socket for heater plug is required, among other factors.

**Pumps for the Evaporation of Organic Vapours.** In rotary oil pumps generally the vacuum obtained is that of the saturation vapour pressure of the oil used. If water vapour or vapour of organic solvents are drawn into the pump the oil becomes contaminated and the final vacuum is lower. The water and solvent vapours are condensed in the compression stroke or stage in the pump and are not ejected as vapour. The condensed vapours consequently mix or are dissolved in the oil. The condensation of the vapours may be prevented by heating the pump so that the saturation vapour pressure of the vapours is not reached during compression preparatory to exhaustion to the atmosphere. In some cases this is not desirable. The 'Gas-ballast' pump of Gaede may be used in other cases.<sup>1</sup> In this type of pump the condensation of, for example, water vapour is prevented by the dilution of the compressed gases with air during compression. The air is not, of course, drawn through the evacuated apparatus. These types of pumps are of advantage in the

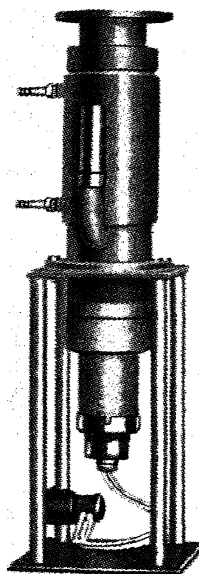


FIG. 29 (VII)

<sup>1</sup> Both heated and 'Gas-ballast' rotary oil pumps are supplied by Firma E. Leybold's Nachfolger.

distilling of solvents from materials at reduced pressure or for the distilling of the last traces of solvent from solvent extracted substances.

In one of the models supplied by Firma E. Leybold's Nachfolger the final vacuum is 1 mm., while in another this is 0.01 mm. Where distillation or evaporation under lower pressures is desired a vapour diffusion pump with a 'Gas-ballast' pump as a fore pump may be employed. Apiezon oil diffusion pumps will rid themselves automatically of impurities of the order of volatility of benzene, acetone, or alcohol. Askew and Bourdillon<sup>1</sup> describe a method for the mechanical removal of contaminated oil from the pump. This consists in fitting a discharge trap on the top of the rotary oil pump (see Fig. 30 (VII)). The main oil reservoir of the pump is shown at A, while B

depicts the ball-valve at the exit from the pump. The trap (represented by shaded portion of figure) consists of a rectangular brass box, C, fixed to the body of the pump using a lead gasket, D.

The oil level is kept at that normal to the pump by an overflow tube, H, with a constriction, J, which prevents undue loss of oil when the levels are disturbed by large volumes of air passing through the pump. A baffle-box, F, is used to retain oil thrown up with the escaping air. G is a bent tube designed to prevent such traces of oily spray as escape from F from reaching the pump driving belt, and so causing slip. This is only needed when much air is passed through the pump, and is recommended to be a loose fit in the neck of F, so as to allow of the pouring of oil into F when desired.

A narrow copper pipe, E, is connected to a water pump (or an evacuated vessel) so that the oil in the box, C, can be drained away when contaminated. It reaches to within a few millimetres of the ball valve of the pump. When evaporating large quantities of a solvent it is advisable to add an oil reservoir, such as is shown at K, to the vacuum line. By this means oil can be admitted to the pump from time to time to maintain the lubrication, which otherwise suffers from the removal of oil.

The designers carried out a number of tests with this arrangement in order to determine how quickly a vacuum of 0.1 mm. of mercury or less could be reached after the oil in the box had been thoroughly contaminated by evaporating various solvents through the pump. In eight such tests, in which 50 ml. of ether were evaporated in a 5-litre bottle, a vacuum of 0.1 mm. was reached after times varying from 17 to 23 minutes. The pressures were

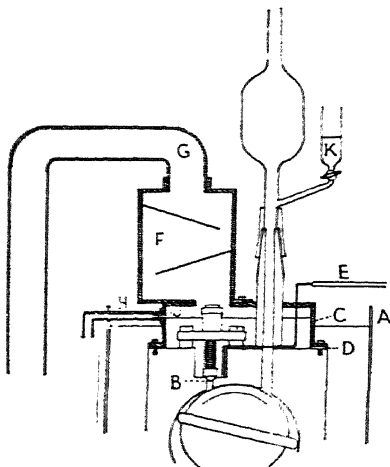


FIG. 30 (VII)

<sup>1</sup> *J. Sci. Inst.*, 1932, 9, 280.

measured with a multi-range McLeod gauge, which was protected with a  $P_2O_5$  bulb, and was cut off from the rest of the system by a tap until most of the vapours had been pumped out. To ensure that the readings were not seriously affected by condensable vapours, comparison readings were taken with a discharge tube, calibrated on dry air, and the gauge readings were on occasion repeated, at different compression ratios. A typical test quoted by the designers (*loc. cit.*) gave the following results, when evaporating from a system the volume of which was about 7 litres.

Fifty millilitres of ether were evaporated through the pump in a period of 6 minutes. Thereafter the pressure fell as follows :

	Time minutes	Pressure mm.	Discharge tube—length of Crookes' dark space mm.
Pump stopped, oil drained from box, box refilled with oil . . . . .	1	Not measured	—
Pump restarted . . . . .	5	—	—
	6	2.25	1
	8	0.99	3
Pump stopped, oil drained from box, box refilled with oil . . . . .	9	—	—
Pump restarted . . . . .	13½	—	—
	14½	0.36	5
	15½	0.16	7
	17	0.10	10
	19	0.09	10

Similar results were obtained after evaporating alcohol, acetone and benzene. Three tests were continued to lower pressures. In two of these, 0.05 mm. was reached after a total of about 35 minutes from the start, but the lower pressure of 0.02 mm., of which the pump was capable, was only reached after considerable further periods.

These results were obtained with a pump and trap that had been in constant use for over 2 years. The designers pointed out that a much more rapid fall of pressure could probably be obtained by moving the crossbar, L, above the ball valve, so as to allow of the use of a smaller box, C, that did not surround the pump inlet. In the particular work of the designers distillation in a high vacuum was performed, using a two-stage mercury-vapour pump in series with the oil pump. The substances concerned (preparations of vitamin D) were introduced into the still in solution in alcohol or ether, and the mercury pump was only heated after nearly all the solvent had evaporated. This method was found convenient and efficient.

**The Use of Activated Charcoal.** Although some form of pump is generally to be preferred for the production of low pressures, there are occasions when it is convenient to make use of the adsorptive properties of activated charcoal. The usual method of preparing the charcoal is as follows: A sufficient quantity of soft coco-nut kernel is heated in a muffle furnace for several hours to just below red heat, until no more vapour is

evolved. The temperature is then raised to a dull red heat for half a minute. The charcoal thus prepared is introduced into a tube and heated in a bath of molten sulphur for several hours while the tube is evacuated. When the heating is judged sufficient the tube is sealed and the charcoal may then be kept until required. The hard shell of the coco-nut may be treated in a similar fashion, and is said to possess superior adsorptive powers.

For use the activated charcoal is placed in a small bulb or tube sealed on to the main vessel and cooled in liquid air. Its adsorptive powers vary widely with its mode of preparation and previous history, and it is difficult to do more than indicate what results may be expected from a given sample.

To give an idea of its capabilities, Blythswood and Allen found that 216 grams of charcoal cooled in liquid air reduced the pressure in a bulb of 925 ml. capacity (containing air) from 40 mm. to 0.0009 mm. of mercury in 3 hours.

Table A shows the selective action of charcoal on different gases. The volumes adsorbed are measured in ml. at 760 mm. of mercury pressure.

TABLE A

Gas	Volume adsorbed at 0°	Volume adsorbed at - 185°
Helium . . . .	2 ml.	15 ml.
Hydrogen . . . .	4	35
Argon . . . .	12	175
Nitrogen . . . .	15	155
Oxygen . . . .	18	230

Activated charcoal can be used again and again indefinitely, provided it is heated *in vacuo* after each adsorption to remove the occluded gases, and, in fact, to do so improves its adsorptive powers up to a certain limit. The optimum temperature for this treatment is 650°.<sup>1</sup>

**General Remarks on Exhaust Procedure.** Connecting tubes should be short and of wide bore as the throttling effect of long and narrow tubing is considerable with consequent reduction in the speed of pumping. The 'Cenco Conductance Chart' is useful in this connection for finding the conductance of air in tubes at low pressures. Transfer of gas in connecting tubing at low pressures takes place principally by diffusion. The rate of transfer decreases rapidly with the diameter and length of the tube. The chart is made up of a set of graphs based on Knudsen's equations<sup>2</sup> and which gives the conductance when the radius and length of the tube have been ascertained. It is of use in determining the speed with which a system may be exhausted to a predetermined pressure.

Gases occluded on the interior surfaces of an evacuated vessel cause an appreciable rise in pressure after sealing off. This can be obviated to a certain extent by baking the vessel for an hour or two during exhaust at as

<sup>1</sup> Lemon, *Phys. Rev.*, 1919, 14, 281. Lemon and Blodgett, *ibid.*, 1919, 14, 394. See also Becker and Jaycox, *Rev. Sci. Inst.*, 1931, 2, 773.

<sup>2</sup> *Ann. d. Phys.*, 1909, 28, 75, 999.

high a temperature as is practicable. The highest permissible temperatures vary with the quality of glass. The following table will serve as a guide :

Lead glass	360°
Lime glass	400°
Pyrex glass	500°

These limits may be increased by about 100° without fear of the vessel collapsing, if the oven in which the baking is done is itself exhausted to a pressure of about 5 mm. of mercury.

Metal parts also occlude undesirable gases. They should be washed in acetone and alcohol to remove any surface grease, thoroughly dried, and heated separately in a vacuum oven. The heating may be done by the passage of an electric current or by electronic bombardment. Rubber should not, in general, be used in a high vacuum system where the pressures are of the order of 0.01 to 0.001 micron.

Mercury vapour and other condensible gases may find their way to the exhausted vessel from the greased point between the vessel and the pump. They may be eliminated by interposing a refrigerating chamber cooled in liquid air, a suspension of solid carbon dioxide in ether, or solid carbon dioxide alone. The two latter agents will not entirely eliminate water vapour, and it is therefore advisable to insert a vessel containing phosphorus pentoxide between the rough and fine pumps when they are used. When exhausting to very low pressures it is preferable to cool with liquid air evaporated under reduced pressure.

The occurrence of leaks in evacuated glass apparatus may be searched for by passing an insulated electrode of a Tesla coil (with one end earthed) over the apparatus. The existence of a leak is shown as a bright spot where the discharge enters the evacuated apparatus. For the control of pressure in an evacuated apparatus a calibrated leak in the form of a needle valve may be employed.



## SECTION 2: OSCILLATING PUMPS

The problem of circulating gas in a closed system is one often met with in research work in the physico-chemical laboratory, and from time to time descriptions of various devices for this operation have appeared in scientific literature. Of the many types of pump available for this purpose a column of mercury oscillating in a U-tube appears to be the most suitable. There are several pumps utilizing this principle, the essential difference between them being the method employed in keeping the column of mercury in oscillation. Bone <sup>1</sup> used a reciprocating air pump as a source of energy.

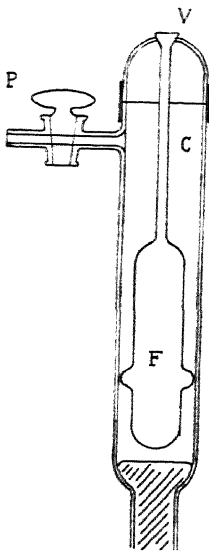


FIG. 31 (VII)

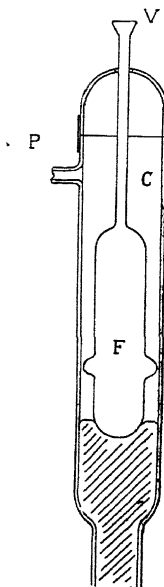


FIG. 32 (VII)

Pearson and Thomas in their pump <sup>2</sup> further utilized the oscillatory motion of the mercury column to apply the principle of the hot-air engine. The free leg of the U-tube is closed by a hard glass or silica bulb heated by a Bunsen burner. The alternate compression and expansion of the gas in this hot bulb converts some of the heat into sufficient energy to keep the mercury in motion. In another pump described by Chatterji and Finch <sup>3</sup> the free

<sup>1</sup> *Proc. Roy. Soc.*, 1919, A 96, 126.

<sup>2</sup> *J. Chem. Soc.*, 1925, 127, 2450.

<sup>3</sup> *Ibid.*, 2464.

surface of the mercury column is alternately depressed and released by a loosely fitting plunger operated by a geared-down electric motor.

The mercury oscillating pump described below,<sup>1</sup> though simple in construction, has given satisfactory results. It can be driven by an ordinary laboratory suction pump.

The principle on which it works can be readily understood from a study of Figs. 31 (VII)–33 (VII). The free leg of the U-tube is closed by a chamber, C, which is connected by the tap, P, to a suction pump. Into the dome of this chamber is ground a glass valve, V, joined by a glass stem to a glass float, F.

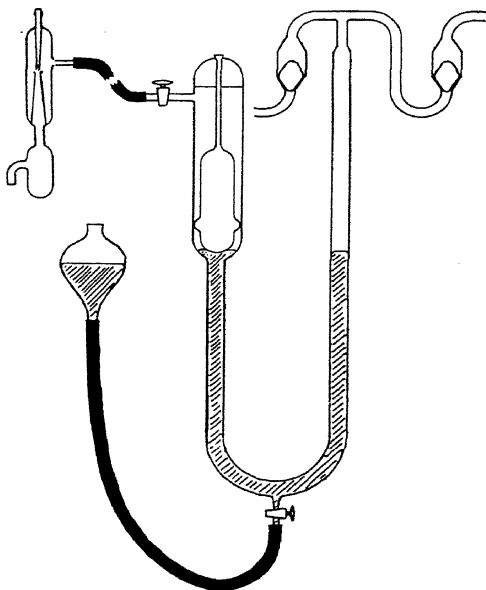


FIG. 33 (VII)

Fig. 31 (VII) shows the mercury at the bottom of a stroke with the valve, V, closed; in this position a partial vacuum is created in the chamber, C, which the mercury tries to fill. As soon as the level of the mercury reaches a certain height, the upward pressure on the float, F, due to the displacement of the mercury, overcomes the downward pressure on the valve, V, which opens as in Fig. 32 (VII). This breaks the partial vacuum by allowing air free access to C. As before the valve lifts, the column of mercury has been raised beyond its normal position, it tends by its own weight to fall back, automatically closing the valve as it does so, and thereby restarting the cycle. A by-pass across the inlet and outlet valves is found in practice to be

<sup>1</sup> Donnelly, Foott, Nielsen and Reilly, *Soc. Chem. Ind.*, 1927, XLVI, 46, pp. 437 T-438 T.

unnecessary. By careful adjustment of the tap, P, and the quantity of mercury run into the U-tube from the reservoir, any speed of gas circulation within the limits of the pump may be maintained, also by leaving the mercury reservoir open to the U-tube the pump will automatically adjust itself to a positive or negative alteration of half an atmosphere pressure in the closed system (Fig. 33 (VII)).

It has been found by experiment that for smooth and reliable working, the ratio of the cross-sectional areas of the valve, V, and the float, F, should not exceed 1:10.

Lateral movement of the float must be prevented if the valve is to sit properly, and friction between the float and the chamber reduced to a minimum. This is best done by keeping the internal diameter of the chamber about 0.8 cm. greater than the external diameter of the float, and by the

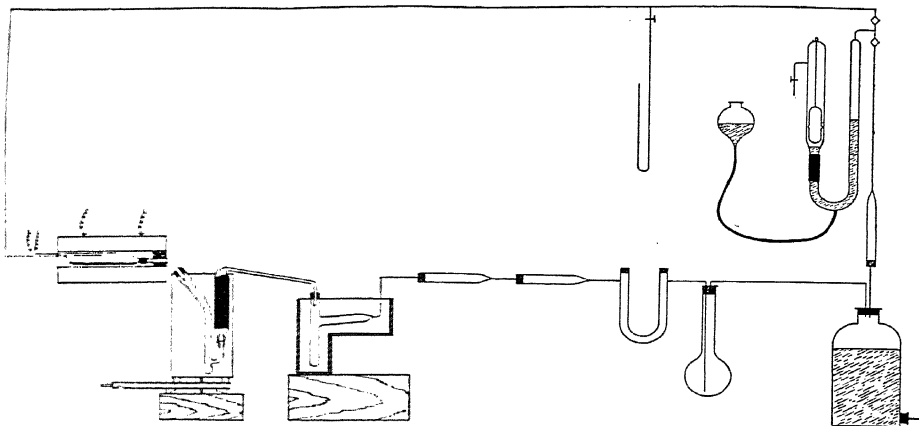


FIG. 34 (VII)

blowing of three small teats on the float. For simplicity of construction the chamber, C, may be made in two sections with ground edges and bound in position with adhesive tape.<sup>1</sup>

The following are some particulars of the pump shown.

*Dimensions.* Overall height of U-tube, 50 cm.; bore of U-tube, 0.8 cm.; distance from bottom of float, F, to top of chamber, C, 22 cm.; internal diameter of chamber, C, 2.4 cm.; external diameter of float, F, 1.6 cm.

*Performance.* Maximum circulation against a pressure of 9 cm. of water was 66 litres per hour; minimum circulation against a pressure of 9 cm. of water was 0.15 litre per hour; working against a positive or negative pressure of 16 cm. of mercury the circulation was 5 litres per hour.

Fig. 34 (VII) shows a typical closed circuit containing a mercury oscillating pump.<sup>2</sup> This circuit is suitable for the distillations of small samples of coal or peat in a gas, e.g. nitrogen or air. The fuel, to quote a particular

<sup>1</sup> The apparatus can be supplied by Messrs. Griffin, London.

<sup>2</sup> Donnelly and Reilly, *Sci. Proc. Dub. Soc.*, 1930, 19, 29, 374.

example, is placed in a glass retort, the retort being encased by a small electric furnace. A first condenser is kept at a temperature of  $120^{\circ}$ , and condenses tar with a boiling point under  $120^{\circ}$ . One tube of glass wool is used to trap the 'tar fog'. Water and light oil are condensed in a second condenser at  $-20^{\circ}$ , a tube of tightly packed glass wool ensuring that no trace of fog remains uncondensed. A type of compound is evolved during coal or peat distillations that can be absorbed by phosphorus pentoxide, and this is removed after the vapours have passed through the cotton-wool. Light spirit is removed by a U-tube of activated carbon, which is dried to constant weight in a current of dry air at  $105^{\circ}$ . The scrubbed gas, after leaving the activated carbon, passes through a mixing flask, and finally to a gas reservoir. This consists of a two-litre bottle fitted with a tap at the bottom and a three-holed rubber bung at the top. A burette connected to the lower tap enables mercury to be run into the reservoir, while a special tap leading from the top is used for sampling the gas. After leaving the reservoir, the scrubbed gases pass through a guard tube of phosphorus pentoxide and asbestos fibre (this is a precaution against moisture from the mercury being carried into the circuit), and are pumped by means of the special mercury oscillating pump over the peat in the retort. A liquid paraffin gauge between the pump and the retort indicates the pressure in the circuit, which is kept at atmospheric by adjustment of the mercury in the reservoir.



## CHAPTER VIII

### VARIOUS OPERATIONS

#### SECTION 1: GLASS-BLOWING

**S**UCH problems as glass-blowing and laboratory manipulation generally, including silvering of glass, working of fused silica, mounting cross-wires in microscopes, construction of resistance coils and general workshop practice require more than mere description for successful accomplishment. The general operations of the physical-chemical laboratory are best considered in connexion with particular processes and experiments, and the various chapters should be consulted for particular points. There are a few items, however, which do not come under the general classifications, and these are considered in this section.

In the physico-chemical laboratory the need for an efficient glass-blower often arises. For simple operations the ordinary worker can generally carry these out himself. The following notes have been written in part by J. L. Buckley.

In the operations described below it is assumed that the worker has access to the common appliances of glass-blowing. They are a blowpipe of the Herrepath type, sharp file and glass knife of glass-hard steel, a large turn-pin, polished and rust-free, carbon or metallic cones, flat carbon plates, and a long piece of thick rubber tubing for blowing. An annealing oven is required occasionally and a large sheet of asbestos acts as a heat reflector. For special work, e.g. with hard glasses or quartz, various types of oxy-acetylene or oxygen-coal gas burners are available with flexible arms and adjustable flames. The Hoke Scorpion 'Cross-Fire' Oxy-gas burner is one of this type.

The ordinary blowpipe has an annular gas outlet which projects some millimetres beyond an axially placed clean inner tube for air or oxygen. The supply of gas and hence the size of the flame is regulated by a lever at the back of the gas tube. An even prolonged air pressure in the inner tube is maintained by a slow movement of the foot on the pedal of a foot bellows. The air pressure is correct when the flame's tip is coloured purple. The flame then consists of an inner core, A, of air which is covered by a light blue, the hottest zone, B, of burning gases. The outer dark blue zone, C, contains the products of oxidation (Fig. 1 (VIII)). The flame (Fig. 1 (VIII), I) is the result of limiting the supply of gas and increasing the blast of air. On reversing the conditions the shape shown in Fig. 1 (VIII), II, is obtained. Generally the flame should be slightly larger than the article being heated.

The best results in glass-blowing are obtained by avoiding undue haste

in manipulation and by a meticulous planning beforehand of the method and arrangement of the necessary appliances. Usually the heavier portion of the work is carried on the left hand and the art of uniformly rotating both

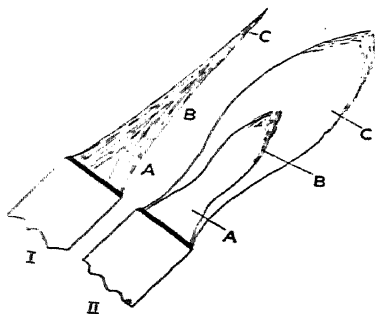


FIG. 1 (VIII)

parts needs mastering. Glass should be first cleaned with a solution of potassium dichromate in concentrated sulphuric acid, washed several times with tap water, once or twice with distilled water and finally with alcohol. It then dries rapidly in a current of hot air. Blowing is done out of the flame only and then after a momentary pause to enable the thinner walls to attain a lower temperature. Thus uniformly thick walls ensue. The article is gradually introduced into the flame to ensure a constancy of temperature whatever the variation in thick-

ness, and is rotated before the light blue zone until sufficiently hot for easy blowing. A piece of work may not cool during stages while attention is required for another piece. It is kept hot in an auxiliary flame.

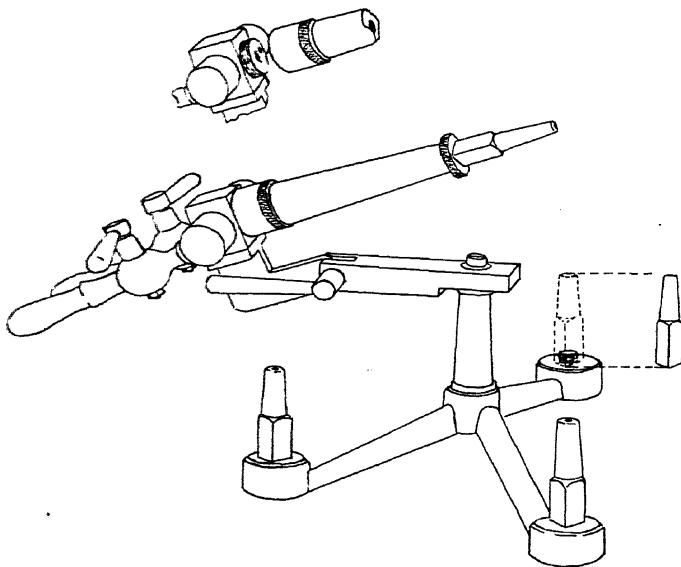


FIG. 2 (VIII)

In Fig. 2 (VIII) is shown, in outline, a modern form of blowpipe for bench use. A number of different size nozzles or jets are provided for the production of flames of different sizes and when not in use these can be fixed to the

base of the tripod. The blowpipe can be rotated about vertical and horizontal axes and can be used independent of the tripod base. Air or oxygen and coal gas have a mixing chamber and can also be made to mix by means of a by-pass in the tube leading to the jet.<sup>1</sup>

**Annealing.** This is a process of slow cooling to avoid subsequent fracture. All parts of the worked glass are heated to just below softening-point in a fireclay or metal oven and then slowly cooled to room temperature. The time during which the work is maintained hot, and the time of cooling, depends on the thickness of the glass components. Two hours' heating and up to 8 hours' cooling are required for large solid glass stoppers. The time allowed in either case allows all parts of the article to reach the same high temperature and then a uniform temperature in cooling is also achieved. Soda-glass requires more annealing than lead-glass.

**Types of Glass.** (a) Soda glass: this is the usual type supplied by manufacturers when the order is unspecified. Its composition is sodium silicate with small percentages of aluminium and calcium or potassium silicates. Its drawbacks are that it becomes mobile suddenly and infusible when old (devitrification) and it requires slower heating and annealing. Also it is liable to spontaneous cracking.

(b) Lead-glass is also called flint-glass and has only limited application. It consists of calcined crushed flint with lead silicate. It melts easily but slowly, thus facilitating its working, and is stable and free from spontaneous cracking. However, the light blue cone blackens it. This defect is also produced by yellow ammonium sulphide, and some chemical reagents attack it. The discoloration may, however, be removed by heating in the outer tip of the flame.

(c) Combustion glass has more calcium and potassium silicates than soda-glass. Being less fusible it requires oxygen in the blowpipe but has a longer viscous stage.

(d) Resistance glass, so called because it is the least soluble, is useful where the dissolving of the alkali and silicate content of the containing vessel would interact with the liquid contained in it. This glass contains calcium and magnesium and is harder than soda-glass.

#### CUTTING—LEADING A CRACK—MARKING GLASS—DRILLING

(a) **Cutting.** Thin tubing up to 8 mm. external diameter and 1 mm. thickness is severed by incising a notch with a sharp triangular file used with some pressure. The thumbs are placed in contact diametrically opposite to the notch and used as a fulcrum for the inward pressure exerted by the hand. This should produce a square end cut. A similar result is obtained by heating and drawing off the tube at the point where it is desired to cut it. The tube is now sealed and heated till it fuses and then blown strongly. A filmous kidney-shaped bulb results which when removed with a file leaves a true square end cut. For thicker tubing of larger diameter a red-hot bead of glass is applied to one of two file notches made perpendicularly to the axis

<sup>1</sup> Mr. Niedergesäss, the Cavendish Laboratory (Cambridge) glass-blower, has made one of these blowpipes for the authors—and can supply others.



of the tube. An instantaneous fracture results, while the end may be improved by filing.

(b) **Leading a Crack.** This is the method applicable to large tubes or bulbs. A crack is produced by application of a red-hot rod to a file notch and the hot lead is then placed 0.05 cm. from the end of the crack in the required direction.

(c) **Marking of Glass.** The best results are produced by etching. The vessel is coated thinly with molten paraffin wax and the wax when cool is marked as required with a needle point. This side of the object is then held over hydrofluoric acid vapour for about an hour, or if a deep incision is necessary the liquid acid is applied for some minutes. The wax is then melted or dissolved off.

(d) **Drilling Glass.** This operation is usually only called into use in making a glass stopper. A rod of hard steel with its end irregularly broken serves as a drill which is rotated at high speed with a solution of camphor in turpentine as lubricant. The drill needs initial guiding to prevent it straying over the surface of the glass.

**Drilling Holes through Glass.** According to Bayliss a suitable tool for drilling a hole having a diameter of a quarter of an inch or more, through plate glass, is a short piece of copper tube, used in conjunction with turpentine and powdered emery or carborundum. The tube, which should be about 2 inches long, and slightly less in external diameter than the size of the hole required, is connected to a metal shank, and then fitted to an ordinary brace or drill-stock (Fig. 3 (VIII)).

The connection may be made somewhat flexible by 'packing' the copper tube as shown in the sketch, where A represents a wooden plug, B a cushion of soft rubber, and C a section of rubber tubing sufficiently stout to grip the metal shank D.

The glass is laid upon a level table, with a few sheets of newspaper beneath it, and the position of the hole to be drilled is clearly marked, say, with a spot of dark paint.

For a more substantial guide for the drill, a hole is first bored through a wooden block to receive the tube. This block is then laid upon the glass in the appropriate position, and clamped down by any convenient means.

Very little pressure should be applied to the brace. The tube should be kept generously supplied with turpentine and carborundum, and should be lifted occasionally during the drilling, so that a fresh supply of the abrasive may reach the surface which is being cut.

(VIII)

A small hole, up to say an eighth of an inch, can be drilled through a glass vessel, such as a beaker for laboratory use, with a watch-maker's graver. This tool, which is made of hard steel, is of diamond section, i.e. a rhombus, and is ground diagonally from one corner to the other to a fine point.

With a very slight pressure, the surface of the glass can be pierced by one or two turns of the point, and a hole can be drilled through the beaker by hand in about 10 minutes. The graver should be kept wet with turpentine.

As the cutting edge of a graver is out of the centre, care must be taken to see that it does not function as a lever, and so chip the glass.

A suitable liquid for grinding glass consists of turpentine (3 parts), gum camphor (2 parts), ether (1 part). For grinding glass this is used with powdered emery. For fine polishing a sheet of emery with this liquid may be employed.

**Sealing a Tube** (Fig. 4 (VIII) ). The tube a few centimetres from one end is gradually let into the blowpipe flame in front of the light blue zone and rotated constantly about both ends. The longer end is held in the left hand and the tube is moved slightly towards the right and then drawn apart in the flame and sealed. The axial movement diminishes the bulk of the inevitable blob at the seal. The seal is then slightly expanded, reheated till sagging and gently blown to a hemispherical end and annealed in a smoky flame. The dotted line in the diagram indicates position of the seal.

**Specimen Tube for Solid or Liquid Preparation.** A tube is sealed hemispherically and contains the solid to half an inch of the open end. This is drawn out and fused as a conical seal. A modification is needed for a liquid. The open end is first drawn off a few centimetres from the top to give a connecting capillary. The liquid is placed in the open end of the tube, held vertically and the entrapped air released by pushing a long narrower capillary tube down into the air chamber. The liquid pressure above forces the air up the capillary and the lower tube is thus filled two-thirds. This portion is then sealed at the junction of the cone and the capillary tube (Fig. 4a (VIII) ).

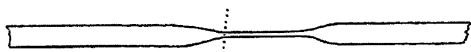


FIG. 4 (VIII)

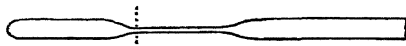


FIG. 4a (VIII)

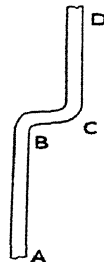


FIG. 5 (VIII)

**Bending Tubes and Spirals.** A narrow tube may be bent to any angle in one operation. A length of 3 or 4 diameters is held in a batwing burner and then removed from the flame, and after a pause, bent slowly. By reheating and blowing the flattening at the bend may be rounded. Large tubes are bent perpendicularly in several stages, a small bend being got after each heating and the danger of flattening is obviated by maintaining the air pressure inside.

A spiral may be formed by bending as above and winding the softening tube round an asbestos-lined copper mandrel slightly conical in shape to facilitate withdrawal (Fig. 5 (VIII) ). It may also be made by hand. One end of a tube is sealed as at A and 4 inches from this at B, a right-angled bend effected. This is the axis of the spiral, and it forms the axis of rotation for the left hand. A second right-angled bend equal to the proposed radius

## PHYSICO-CHEMICAL METHODS

of the spiral is then made a  $\pi$ , so that the three portions of the tube are uniplanar. Along C.D. a piece of tubing greater than the length of the flame is heated by a combination of rotational and to-and-fro motion. This is held erect after removal from the flame and is shaped by a slow clockwise twist with both hands. About one-third of a loop is thus got. The latter process is repeated to give the complete spiral.

**Joints.** It is essential to have square cut ends in tubes intended for joining in order to avoid air gaps. In joining a narrow tube to a wider one the principle employed is to evolve from the wider tube a small projecting tube equal in diameter to the smaller one.

(a) *End to End Joints of Equal Tubes.* An end of one tube is closed by a cork or sealed and a small lip is turned out at the other end, and this is kept hot in an auxiliary flame. One end of the other tube is spun similarly and both lips are heated simultaneously to softness and rotated one in each hand and complete contact between the two soft ends established by gentle pressure. The conjoint tube is then blown to an oval shape and reheated till the junction sags to less than the diameter of the tubes. They are then

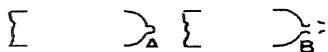


FIG. 6 (VIII)

gently pulled apart and blown out slightly in uniformity. Inequalities of thickness are removed by reheating till the glass runs together and then reblowing.

(b) *Unequal Narrow-Walled Tubes, e.g. a Pipette.* A hemispherical seal is made at one end of a large tube. The narrow hot blowpipe flame is applied to the centre of this and enables the operator to blow a small bulb of the same diameter as the smaller tube (A) (Fig. 6 (VIII)). The same flame softens the tip of this bulb, which is then blown out and cleaned of glass shavings as in B, giving a fairly square cut. The procedure then is the same as in (a).

(c) *'T' Piece.* Using the small narrow hot flame a bulb of diameter just less than the leg of the 'T' piece is blown in the side of the cross-piece and the rest of the manipulations are identical with those of (b).

**Bulb Blowing.** Some general considerations apply to all classes of bulbs. They are (1) the collecting and working of sufficient glass to form a thick stable bulb; (2) a waist at the junction of the hot glass and solid tube is inhibited by heating with the axis in a vertical position against an inclined flame; (3) blowing must be done with the tube's axis horizontal and it must be rotated at the same time to ensure perfect roundness; (4) unequal expansion is corrected by holding the more expanded side to the upward cold current of air. The latter is heated and rises and hence the temperature of the under side is lowered relatively to the upper side. This is only a momentary operation and on renewing the blowing the upper side expands more and a spherical bulb results. Small bulbs present no difficulty in view of these instructions.

(a) *Making a Thermometer.* To make the bulb, one end of a capillary tube is sealed, 1 cm. length at this end is heated. Dry air compressed from

an india-rubber blowing ball keeps the capillary open while heating. The size of the bulb will depend on the coefficient of expansion of the liquid and the range of temperature.

To fill and seal the thermometer a small funnel containing more liquid than necessary to fill the bulb is attached to the top of the capillary tube. The enclosed air is expanded and enables some liquid to be sucked into the bulb. This when boiled eliminates all the residual air if the capillary tube is kept above the liquid's boiling point by an auxiliary burner. The liquid now sucked in fills the tube and the funnel is removed. The liquid is heated just above its proposed maximum temperature and when the liquid recedes the end is drawn off and the liquid reheated to fill the capillary tube, which is then sealed. The thermometer then contains the liquid and its vapour only.

(b) *Large Bulb from a Small Tube.* The collection of sufficient glass is achieved by blowing successive bulbs along the tube and uniting them or by fusing a length of wide thick tubing to the end of a small tube. This addition supplies the material for the bulb. A thistle funnel is an example of such a bulb. To make it a large thick bulb is first blown at the end of an 8-mm. tube and its end is blown off and spun.

(c) *Bulb in the Middle of a Tube.* Insert a thick wide tube in the narrow one or draw out both ends of a thick tube to the same narrower diameter. In either case a large mass of glass is available for the bulb which is blown by sealing one end and rotating the two end spindles at the same rate.

**Internal Seal.** This term is applied to a joint consisting of one tube passing through the wall of another or of a bulb. Two methods may be used: (a) in which the tube passing through another tube is sealed on as a single piece, (b) when the inner tube is made in two parts.

(a) A small tube is heated at the point where it is proposed to join it to the outer tube, compressed somewhat and blown slightly as in A (Fig. 7 (VIII)). It is kept hot. A large tube is sealed by a hemispherical bulb and a slightly conical tube produced as at B. This projecting tube must be just wider than the greatest diameter of A. Both A and B are now heated

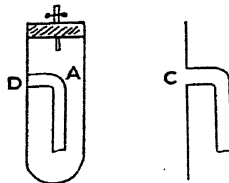


FIG. 7 (VIII)

FIG. 8 (VIII)

simultaneously to just below mobility and the small tube passes through B until A is just inside B. B is now heated in arcs, the temperature of the whole circumference being maintained by occasional rotation, and it falls in and contacts with A. The whole joint is then heated to fusion-point in a fairly large flame and slowly annealed in the flame. It is finished in the sooty flame. The method of annealing must be slower than usual to allow for thickness of joint.

(b) The second method is used in the double-surface condenser. A right-

angle bend A is kept in the flame while the outer surface of the wall of the vessel is heated with a narrow flame (Fig. 8 (VIII)). By the use of a forceps A is placed in position inside this hot region and complete contact made. The wall at D is now blown out as shown at C, and B, a piece of tubing similar to A, added on.

In either case any air-holes are sealed by touching with the soft red-hot end of a narrow rod. When a tube is internally sealed at both ends, a bulb or spiral should be placed in it to relieve the strains which set in on cooling.

**Sealing in Platinum Wire** (Fig. 9 (VIII)). A bead of lead glass is applied around the wire. A small projecting tube is blown in the side of the tube and the lead-glass bead has a maximum diameter just less than the diameter of this outlet. The bead is sealed in as in working an internal seal.

**Uses of Glass Rod.** (a) *Stirrers* are easily made from glass rod, the only essential features being thorough fusion before jointing and annealing in a smoky flame. Flat carbon plates are used for shaping the soft glass.

(b) *Glass Rod Foot* (Fig. 10 (VIII)). A piece of glass rod is attached to the end of a piece of glass tubing which is blown into to expand the foot slightly. The tube is severed at the dotted line, near the joint, and all the edge of the fracture heated and turned back to form a lip by rotation with a turn-pin. The latter is coated with paraffin wax which prevents the glass adhering to the metal and which also acts as a lubricant. Repeated heatings and spinning against the turn-pin forces the lip of glass back to form a base almost as flat as the base of a wineglass. Across a quarter of this base, heated to redness, a red-hot long rod is drawn till it adheres. It is then



FIG. 9 (VIII)

FIG. 10 (VIII)

FIG. 11 (VIII)

FIG. 12 (VIII)

drawn away and detached and the projecting legs flattened between carbon plates. Two other legs are added in the same manner and the whole piece is annealed in a sooty flame.

(c) *Glass Tap to Fit a Socket* (Fig. 11 (VIII)). A red-hot piece of thick rod is compressed at one end to give a mass of glass of the shape of A. It is reheated and drawn out to give an approximate conical shape of the same size as the socket. The top axis is then drawn off and to this end a glass tube, closed at one end, is joined, the closed end being tapered off. The joint is well fused, while air pressure is maintained inside the hollow tube, by rotation around the lower axis of the rod. The lower portion of rod is then drawn off and the rough stopper ground to an approximate shape in a copper cone of the same dimensions as the socket with a rough abrasive (Fig. 12 (VIII)). The hole is then drilled through the plug and the grinding repeated with finer grades of abrasive material. During the grinding process the plug is lifted to allow a fresh supply of abrasive to get down and in order to clean the orifice.

## SECTION 2: MANIPULATION OF PYREX AND QUARTZ

### PYREX GLASS <sup>1</sup>

**Lampworking of Pyrex Brand Glass.** Since the introduction of Pyrex brand laboratory glassware an increasing number of uses have been found for pyrex brand glass, one of the most important being its use for the construction of scientific apparatus for which it is particularly suitable.

Because of the ease with which pyrex brand glass can be manipulated in the blowlamp it is especially suitable even for the beginner in laboratory glass-blowing, and by exercising a certain amount of patience quite complicated pieces of apparatus can be constructed.

The methods of glass-blowing outlined in the previous section are the same as those adopted for softer glasses, but it is necessary to explain some of the equipment and processes that apply only to pyrex brand glass. This glass softens at a much higher temperature than ordinary soft glass. It is therefore absolutely essential that the blowpipe should be enriched with oxygen; an ordinary air and coal-gas blowpipe can be used, and the oxygen introduced through a T piece into the air line. Great care should be taken to see that the pressure of oxygen does not exceed the air pressure as it would cause a backfire in the blowlamp. Pressures used by the writer are coal gas (25 cm. of mercury), air (10 cm. of mercury) and oxygen pressure to suit the experiment. The glass softens quicker than ordinary glass on removing from the flame and therefore manipulation with pyrex should be more rapid than with soda glass.

**Cutting.** The smaller sizes of tubing up to 25 mm. diameter can be cut quite easily with the ordinary glass knife or file, by making a cut and snapping by grasping the tube with the thumbs pressing on the tubing from the side opposite the cut and pressing both ends of the tube away from the cut, exerting a slight pull at the same time. It will be found that the tube snaps more readily when the cut is wet. The larger-sized tubing should be cracked with a hot wire, i.e. a piece of nichrome resistance wire attached to positive and negative points which go to a resistance. The current is turned on and the wire brought to a dull glow by means of the resistance; the tube is scratched by a diamond and heated on the hot wire. After a few seconds water is applied by means of a small brush, and the tube should crack quite easily.

**Sealing.** The most suitable wire to seal through pyrex brand tubing is tungsten, as the coefficient of expansion is close to that of pyrex brand glass. The wire should first of all be heated in the blowlamp to a dull red heat and a light film of potassium nitrite rubbed over it. All excess potassium nitrite should be removed, leaving only a thin coating of chemical. A small sleeve

<sup>1</sup> Manufactured by James J. Jobling & Co., Sunderland.

of pyrex brand tubing with a wall thickness of approximately 0.5 mm. is slipped on and sealed. More glass is added to the centre of the sleeve to form a bead: a small hole is blown in the apparatus and the bead is thoroughly sealed in. A successfully coated wire becomes an orange colour at the sealing-point. It is possible to join pyrex glass to soft glass by the use of a series of different glasses, differing successively by small increments in their expansion coefficient.<sup>1</sup> A silica-pyrex joint can be made by the method of Keyes and Kraus,<sup>2</sup> but the operation requires skilled manipulation.

**Annealing.** Owing to the low coefficient of expansion, pyrex brand tubing which has been lampworked does not need as much annealing as ordinary soft glass: in fact, if carefully made, it can in many cases be used without annealing other than the annealing in the blowlamp. Although this is so, however, it is more satisfactory to anneal lampworked apparatus, and pyrex brand glass should be annealed at the following temperatures: Bring the temperature up slowly to 550°; hold at this temperature for half an hour, then drop the temperature at the rate of 1° per minute until 500° is reached, after which it may be dropped at the rate of 2° per minute down to 400°. After dropping to 400°, cooling may be allowed to take place more rapidly. If this procedure is followed perfect annealing should be obtained.

### FUSED QUARTZ

Speaking at the Evening Meeting of the Royal Institution of Great Britain on Friday, 8 March 1901, on devitrified quartz, Shenstone said:

Although great improvements have been introduced into the art of glass-making during the last quarter century, glass still remains unsuitable for many of the purposes to which we put it and there is still a real need for some plastic material more infusible, more insoluble, more fully transparent, more plastic and more stable under changes of temperature than glass. Such a substance exists in the form of vitrified quartz or vitrified silica as I shall prefer to call it.

Shenstone was one of the pioneers of the fused quartz industry, his early experiments in its production resulted in the formation in 1906 of a company in London for its commercial manufacture, and owing to continued improvements in manufacturing methods the present-day physicist and chemist is fortunate to have at his command articles of fused quartz in all the variety of shapes normally produced in glass as well as in the form of rod which he can, if he so desires, manipulate himself in the oxy-coal gas blowpipe in a manner similar to that employed for the lower melting-point glasses.<sup>3</sup>

The manipulation of fused quartz tubing and rod in the blowpipe is in many ways easier than the working of soft glass and anyone who has acquired the necessary skill for the production in soft glass of 'T' joints, small bulbs, &c., can after little practice succeed in performing similar operations with fused quartz.

Fused quartz softens at about 1,500°; its melting-point is between 1,700 and 1,800°. It will be obvious therefore that a hotter flame than that given

<sup>1</sup> Taylor and Austin Bailey, *J. Ind. Eng. Chem.*, 1921, 131, 1158.

<sup>2</sup> U.S. Patent 1014757.

<sup>3</sup> The fused quartz can be obtained from the Thermal Syndicate, Ltd., Wallsend-on-Tyne.

by the glassblower's torch must be available. An oxy-coal gas flame can be used, but not all of the flame is hot enough to melt the fused quartz; only that part of the flame situated just beyond the inner blue cone is suitable. What is required is not so much a very large flame as one that presents a very hot spot. Suitable blowpipes for melting fused quartz are lead burning blowpipes obtainable from the British Oxygen Company. For small work such as for melting and closing the ends of tubes up to 0.625 inch external diameter and for making 'T' joints, &c., blowpipe No. S.601 is suitable, and for larger work No. S.1012 should be used. These blowpipes are, however, not suitable for melting quartz as they are received from the makers; the oxygen injector must first be unscrewed from the blowpipe and the fine hole in it opened out to about 0.7 mm. in diameter, and to about 1 mm. diameter for the large blowpipe. This operation is best done with a jeweller's tapered broach. The hole in the injector should be opened out a little at a time and the blowpipe flame tested until it is observed that the inner blue cone is about 0.5 inch long for the small blowpipe and about 0.75 inch for the large one when sufficient oxygen is passing through the blowpipe which will just not extinguish the flame. If the hole is made too large it will be impossible to obtain a suitable shaped inner cone and the blowpipe may be spoiled. Various sized jets may be obtained for both blowpipes and a useful selection to have at hand would be two sizes for each blowpipe; for the small blowpipe the jets should have a 1- and a 1.5-mm. hole, and for the large blowpipe a 2- and a 3-mm. hole.

It is most essential that the fused quartz tubing should be perfectly clean, both inside and outside. Before attempting to work it in the blowpipe flame, it should be washed with dilute hydrofluoric acid (one part acid to about two parts water), followed immediately by tap water and finally in distilled water. It should then be dried out in a warm place such as a drying oven; it is then ready for working.

Unlike glass tubing, fused quartz tubing will not remain soft long enough to permit of it being removed from the blowpipe flame for the purpose of placing the end of the tube in the mouth for blowing. It is necessary therefore to have a suitable length of light rubber tubing attached to one end of the fused quartz tube; the other end of the rubber tube should be attached to a suitable mouthpiece which is held in the teeth so that blowing can commence without any delay; a 30-inch length of pedal cycle valve tubing is ideal for this purpose. When heating the quartz tube the lips must be kept open so that the air in the tube may have free access to the atmosphere and so prevent bursting the softened quartz. Except on rare occasions and in very skilled hands, blowing should not be done when the tube is actually in the flame; the tube should be moved just out of the flame when it is ready for blowing.

Because fused quartz has such an extremely small coefficient of expansion (0.00000054) it does not crack when immediately thrust into the blowpipe flame, so that the operator need have no fear that his half-completed task will suddenly fall to pieces as a result of being too quickly heated at the concluding stages; likewise fused quartz articles do not require annealing as in the case of glass apparatus—this is true, at any rate, for all the more simple apparatus likely to be undertaken by the amateur.

Volatilized quartz will deposit on the tube immediately adjacent to the



parts which have been melted and this can readily be removed by playing the blowpipe flame upon it so as to heat the tube to just below its softening temperature. When fused quartz has been subjected to prolonged heating in the blowpipe flame the surface may become devitrified, and whilst the presence of this devitrified quartz will in most cases only spoil the appearance of the article and will not detract from its usefulness, if however it is desired to remedy the defect, the tube should be placed in a bath containing hydrofluoric acid and water in equal amounts and allowed to remain in it for 3 to 5 minutes, according to the depth of the devitrification. The tube must then be thoroughly washed in tap water and finally distilled water and dried. If, then, the affected parts are melted in the blowpipe flame the quartz will regain its original transparency.

Flanged ends of tubes may be formed by heating a portion of the cut end of the tube and bending it outwards with a thin graphite or carbon pencil. Only a small section of the tube should be heated at one time and by working round the tube in this way a neat and strong flange can be obtained. Lips for beakers, &c., may be formed in a similar manner.

Fused quartz rods and tube up to 0.625 inch diameter can be cut by making a scratch with a sharp file and breaking apart. Tubes of larger diameter should be cut through all round with a thin carborundum wheel, preferably lubricated with water.

When working fused quartz in the blowpipe, blue goggles must be worn, and a suitable kind are those sold for electric welding purposes.

The equipment necessary in the use of fused silica in the laboratory is very well described by Neher.<sup>1</sup> Among other useful technique, he describes the operations of (1) Straightening, (2) Bending, (3) Drawing and shrinking, (4) Joining of fibres and quartz, (5) Mounting of fibres, &c. He gives a simple design for a quartz microbalance.

<sup>1</sup> Strong, *Procedures in Experimental Physics*, Chap. V. Prentice-Hall, N.Y., 1938.

### SECTION 3: CLEANING OF MERCURY

There is one operation specially that needs some description, as it is of special importance in the physical-chemical laboratory especially when gases have to be examined. This operation is the cleaning of mercury which accumulates from time to time.

**Purification of Mercury.** To the physical chemist large quantities of pure mercury are a frequent necessity, and many methods have been worked out for freeing the metal from the impurities, particularly traces of other metals, with which it becomes contaminated in use. The automatic cleansing apparatus of Dixon and McKee is particularly suitable.

The mercury is placed in a cylindrical jar (Fig. 13 (VIII) ) 30 cm. high, 5 cm. diameter, which is closed by a rubber ring through which pass a U-tube and a short tube as shown. The U-tube where it passes through the ring is provided with a glass sleeve moistened with glycerol in which it slides air-tight up and down; the second tube is fitted with a smaller tube which is connected to a suction pump. On turning on the pump air passes through the U-tube, while mercury enters the latter by a small hole in the bottom of the bend. The mercury spray leaving the short leg of the tube strikes against a floating glass cap with which it is provided and falls back into the bulk of the liquid. This jacket has two slots, one at the level at which it floats in mercury, so that there may be free communication between the surface of the mercury inside and outside the jacket.

The air current thus causes a circulation of the mercury in the jar, through the spray, and the metal while passing through the spray is cleansed in about 3 hours of most of the impurities. It is advantageous to pour a little dilute nitric acid into the jar to prevent formation of froth. When this liquid on making alkaline gives a black precipitate, showing that mercury is passing into solution, the first stage in the purification is complete.

The mercury is next washed with distilled water, dried by means of filter paper, and run through a hardened filter paper, with a pinhole at the apex of the cone. It is finally dry-blown in the apparatus described, for 8 hours. Another apparatus which also combines aerial oxidation with the electrolytic interchange which takes place in acid purification has been described by Jones.<sup>1</sup> It is somewhat similar to the above and equally efficient.

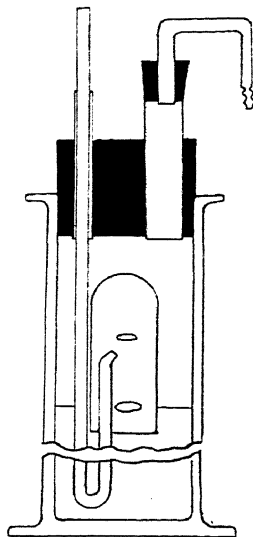


FIG. 13 (VIII)

<sup>1</sup> *J. Soc. Chem. Ind.*, 1930, 49, 45, T. 437.

In another method for purifying mercury (Fig. 14 (VIII) ) the metal is allowed to fall through a long glass tube filled with dilute nitric acid, from the bottom of which it is run off through a capillary bent as shown. Previous purification, by shaking with dilute nitric acid, and a final drying, are necessary.

Evans's purifier (Fig. 15 (VIII) ) has a container for mercury at the top and four tubes sloping as indicated, and containing dilute nitric acid or mercurous nitrate. When the apparatus is working each tube has 0.5 inch

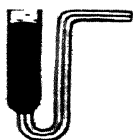


FIG. 14 (VIII)

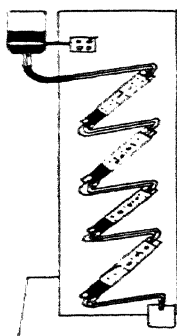


FIG. 15 (VIII)

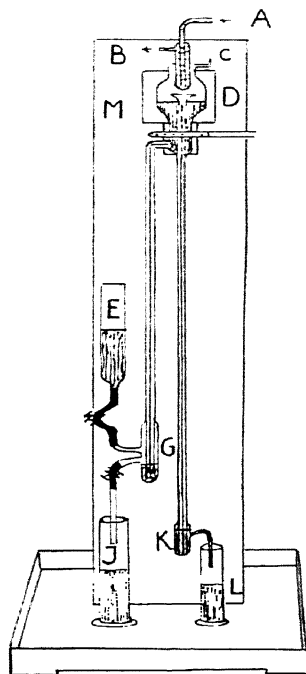


FIG. 16 (VIII)

of mercury in its lower portion and the fresh mercury collects above the surplus and blows it through a capillary (thick-walled) to the next tube.

Another method for the purification of mercury consists in shaking the mercury with its own volume of the following stock solution (water 1,000 ml., potassium dichromate 5 grams, 5–10 ml. of sulphuric acid (60 per cent conc.) ). The shaking is continued until the red mercuric chromate first formed has disappeared and gives place to green chromic sulphate. The powder-like precipitate is washed away with water and the above operation repeated several times. The mercury is then dried.

Dry mercury can also be purified by distillation under reduced pressure, and several types of apparatus are available for carrying out this operation automatically. The one shown in the sketch is satisfactory, since it yields

about 1,000 grams of pure mercury per hour.<sup>1</sup> Mercury is added to the apparatus (Fig. 16 (VIII)) through E, outflows into a reservoir, G, where it rises into the evacuated flask, D, the height of the mercury in which is controlled by the level of G. Any excess of mercury in the latter overflows into J. The flask, D, is heated by a ring burner and contains an internal cup surmounted by a condenser, into which cold water enters by A and from which it flows by B. The volatilized mercury collects on the condenser and falls into the cup, whence it flows to K and siphons into L. The flask, D, is protected by a hood.

Vogels<sup>2</sup> has described an apparatus made of pyrex glass having three capillary barometric tubes suitable for the distillation of mercury under reduced pressure. With this apparatus, which has three capillary barometer tubes, it is possible to work at any desired reduction of pressure, and thus avoid the drawback that at very low pressures some of the noble metals may distil with the mercury. The impure mercury before distillation must be freed from the usual metallic impurities by prolonged washing with mercurous nitrate solution or with ferric sulphate solution. The apparatus is shown in Fig. 17 (VIII). The first barometer tube A is attached by rubber tubing to the reservoir bulb D containing the impure mercury. At the top of this tube is an expansion E (25 mm. in diameter) which is electrically heated by a coil. The vaporized mercury passes into a second expansion F and thence through G and H (where it is air-cooled) into I, and collected in J, from which the purified mercury can be drawn off, without interrupting the distillation. The evacuation of the apparatus is effected through the tube K, the pump being controlled by the tap L. To prevent overheating, an automatic cut-out is provided. The flask D is attached by means of a cord to the counter weight M, the weight of which is equal to that of D when nearly evacuated. When the weight of D becomes less than that of A, a catch O on the rod of the counter-poise, descends and acts on the lever P, which carries a small mercury contact; the circuit is thus broken. The column C is intended to protect the apparatus from the consequences of the accidental admission of air by utilizing the float Q on the surface of the mercury in tube R.

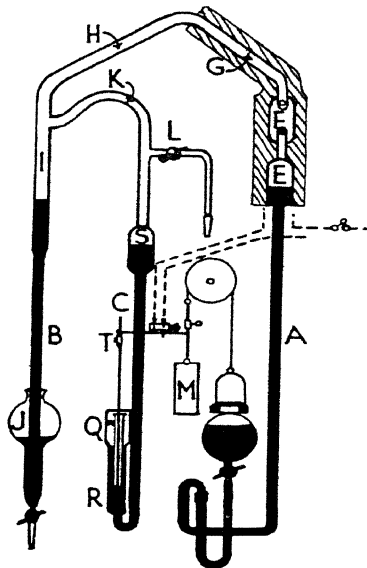


FIG. 17 (VIII)

<sup>1</sup> Made by A. Gallenkamp & Co., London (Lambert design).

<sup>2</sup> *Bull. Soc. Chem. Belg.*, 1934, 43, 327; *Analyst*, 1934, 59, 650.

## SECTION 4: DETERMINATION OF MELTING-POINT

**Introduction.** The melting-point of a solid substance which does not sublime or decompose on heating to its melting-point is one of the best criteria of purity or identity. At a fixed pressure the solid and liquid forms of a substance are in equilibrium at a fixed temperature, and this latter is practically unaltered by the ordinary barometric variations. Further, the presence of even a small trace of impurity almost always alters the temperature of melting, usually depressing it considerably. Some substances may change in crystalline form, depending on the method of heating, and in these cases the employment of the melting-point as an indication of purity may not be so definite.

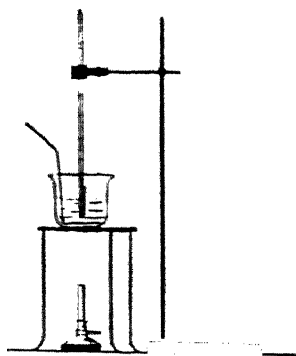


FIG. 18 (VIII)

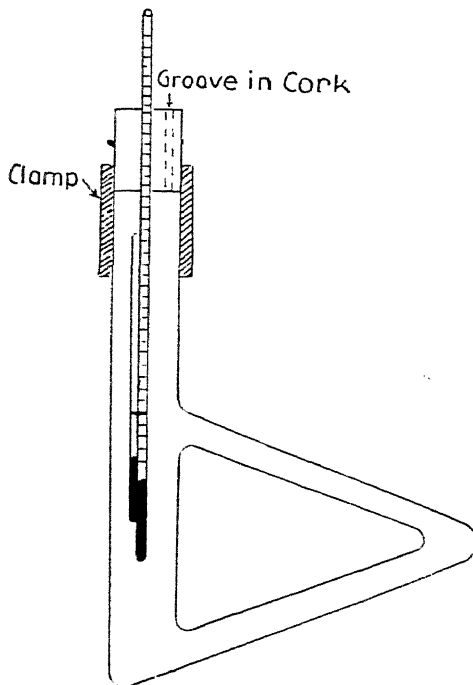


FIG. 19 (VIII)

**Apparatus.** Various types of apparatus employed are shown in Figs. 18 (VIII), 19 (VIII), and 20 (VIII). The powdered substance is placed in a small capillary tube closed at one end, this being accomplished by pushing the open end of the tube into the powder and causing what collects to fall to the bottom by scratching the tube, while vertical, lightly with a file.

The tube is made to adhere to the thermometer by dipping the latter in the liquid composing the heating bath, and then smearing the side of the capillary tube with the liquid clinging to the thermometer. The tube will then remain fixed in position when adjusted as shown in Fig. 20 (VIII); it should be arranged that the substance in the tube is just opposite the bulb of the thermometer.

The latter should have a small bulb to minimize the effect of variation in temperature throughout the liquid in the bath; for the rest it should comply with the specifications laid down for standard thermometers; for accurate work standard thermometers must, of course, be employed.

**Liquid for Heating Bath.** Vaseline, glycerine, or concentrated sulphuric acid are suitable for most substances; the latter is usually employed. Should it become discoloured it can be clarified by adding a crystal of potassium nitrate and heating. For temperatures of  $250^{\circ}$ – $370^{\circ}$ , 30 per cent of potassium sulphate is added to the sulphuric acid. This mixture is solid at ordinary temperatures. For temperatures above  $370^{\circ}$  fused zinc chloride is employed. A mixture of equal parts of sodium nitrate and potassium nitrate also gives a convenient high-temperature bath.

**Melting-point Determination.** A glass screen should be placed between the observer and the apparatus as a precautionary measure. This precaution is especially necessary when dealing with explosive substances. It is also advisable to wear protection glasses when carrying out melting-point determinations. The bath is heated slowly and with vigorous stirring, especially approaching the melting-point. The heating may be carried out by the aid of a small flame or by means of an electrical heating coil. The temperature at which the substance shows the first sign of melting is taken as the melting-point of the substance. If pure, this will be complete usually within a range of  $1^{\circ}$ . Melting-points are generally given as uncorrected; in accurate work the emergent stem correction is employed.

**Melting-point of Wax.** About 0.5 gram is weighed out roughly (first time—afterwards judge by size) and wedged at the top of a hook of platinum wire (0.025 inch diam.) soldered on to the end of a glass rod, which passes through a hole in a cork, fitted into a dry test-tube. Through the cork also passes a thermometer with its bulb near the platinum hook. Slowly heat in water and note melting-point, or melt wax in small beaker (at a low temperature). Then slowly stir with thermometer, cool by holding beaker in the hand until temperature becomes steady for a short period, with solidification of the mass.

**Accurate Determinations.** For accurate determinations a large bath is employed and the liquid in it is mechanically stirred. Approaching the melting-point the temperature is raised, say, at the rate of  $1^{\circ}$  in 5 minutes. The behaviour of the substance is meanwhile closely observed and then the bath slowly heated. A repeat should be carried out and the tube containing

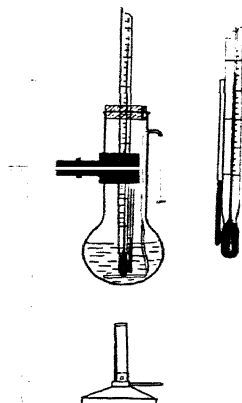


FIG. 20 (VIII)

the substance placed in the bath when the latter is not more than  $10^{\circ}$ – $15^{\circ}$  lower than the previously recorded melting-point.

The use of the fixed temperatures at which pure substances melt to determine a standard thermometer scale is discussed in Chapter X. Reference should also be made to the determination of the 'ice-point' of a thermometer.

A table of corrections for exposed thread of mercury in the melting-point thermometer is also given in that section.

The 'freezing-point' is often an important determination and it is required in many types of analyses. The amount of added water in milk can be determined by this means using Winter's table. The percentage of added water (W) can also be determined from the formula:

$$W = \frac{100(T - T')}{T}$$
 where T is the freezing-point of normal milk (average  $-0.55$ ) and T' the observed freezing-point. The observed values range from  $-0.50^{\circ}$  to  $-0.60^{\circ}$  and the figure is not correlated with age of milk, ash or butter fat but is closely correlated with lactose content.

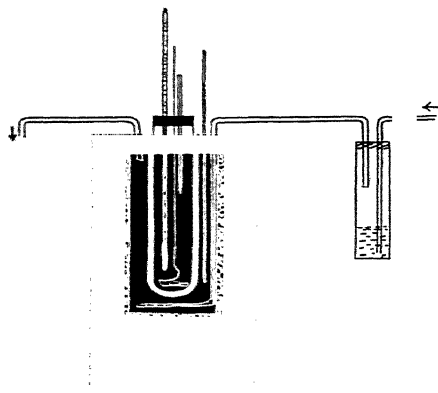


FIG. 21 (VIII)

milk is in exact equilibrium with ice. It gives a figure, however, which is strictly comparable and reproducible with a fair degree of accuracy.

The Hortvet apparatus<sup>2</sup> is shown in Fig. 21 (VIII). It consists of a cylindrical-shaped Dewar flask (1 litre capacity) surrounded by a metal casting. Through the centre is a glass tube 250 mm. long and 33 mm. outside diameter. At one side of the cork is inserted a narrow metal inlet tube, the lower end of which is formed into a perforated loop near the bottom of the flask. At the opposite side is a metal tube of T-shape construction, intended to afford escape for vapours, and also for introducing volatile fluid into the apparatus. At the back portion of the cork is fitted a control thermometer. The freezing test-tube fits closely into the larger tube which is sealed into the cork. At the right side of the thermometer a stirring device is fitted into the stopper. The lower end extends to near the bottom of the test-tube

<sup>1</sup> *J. Ind. and Eng. Chem.*, 1921, 13, 3, 302; Methods of the Assoc. of Official Agric. Chem., 1924; Eimer and Amend Bulletin 396.

<sup>2</sup> *J. Ind. and Eng. Chem.*, *ibid.*

and is provided with a loop, around the outside of which are a number of pointed projections. At the left of the thermometer is a freezing-starter attachment. This device consists of a metal rod, at the lower end of which is an opening for the purpose of carrying a small fragment of ice. At one side of the cryoscope is installed an air-drying arrangement which consists of a Folin absorption bulb inserted through a tightly fitting stopper and extending to near the bottom of a large-sized tube. A short section of glass tubing is inserted through a second opening in the stopper and is connected to the vaporizing tube which enters the cryoscope. Sulphuric acid is poured into the drying tube to a level slightly above the inner bulb. At the opposite side of the apparatus is arranged a drain tube for the purpose of conducting vapours away from the operator. By means of a pressure and suction pump dry air may be forced into the apparatus at a suitable rate, and the mixed vapours conducted out through the base of the drain tube into the sink. An adjustable lens is mounted in a suitable position in front of the thermometer for the purpose of magnifying the scale.

Insert a small-calibre funnel-tube into the vertical portion of the T-tube at one side of the apparatus and pour in 400 ml. of ether previously cooled to  $10^{\circ}$  or lower. Close the vertical tube by means of a small cork and connect the pressure pump to the inlet tube of the air-drying attachment.

Adjust the pump so as to pass air through the apparatus at a moderate rate, as may be judged by the agitation of the sulphuric acid in the drying tube. Continuous vaporization of the ether will cause a lowering of the temperature in the flask, from ordinary room temperature to  $0^{\circ}$  in about 8 minutes. Continue the cooling until the control thermometer registers near  $-3^{\circ}$ .

When the apparatus has once been cooled down to the proper temperature an additional 10 to 15 ml. of ether is on an average sufficient for each succeeding determination. Measure into the freezing test-tube 30 to 35 ml. of boiled distilled water, cooled to  $10^{\circ}$  or lower. Insert the thermometer together with the stirrer and lower the test-tube into the larger tube. A small quantity of alcohol, sufficient to fill the space between the two test-tubes, will serve to complete the conducting medium between the interior of the apparatus and the liquid to be tested. A sufficiently tight connexion between the inner and outer tubes is afforded by means of a narrow section of thin-walled rubber tubing. Keep the stirrer in steady up-and-down motion at a rate of approximately one stroke each 2 or 3 seconds. Maintain passage of air through the apparatus until the temperature of the cooling bath reaches  $-2.5^{\circ}$  and continue the manipulation of the stirrer until a supercooling of sample of  $1.2^{\circ}$  is observed. Manipulate the stirrer slowly three or four times as the mercury column approaches its highest point. Make a duplicate determination and then remove the thermometer and stirrer and empty the water from the freezing-tube. Rinse out the test-tube with about 25 ml. of the sample of milk, previously cooled to  $10^{\circ}$  or lower, measure into the tube 35 ml. of the milk, or just enough to submerge the thermometer bulb, and insert the tube into the apparatus. Maintain the temperature of the cooling-bath at  $2.5^{\circ}$  below the probable freezing-point of the sample. Make the determination on the milk, following the same procedure as that employed in determining the freezing-point of water. The algebraic difference between



the reading obtained on the sample of water and the reading obtained on the sample of milk represents the freezing-point depression of the milk.

A simple apparatus has been described by Monier-Williams,<sup>1</sup> which gives an accurate determination of the true freezing-point of milk, and the original should be consulted for details of conditions. The main features of the apparatus are that, 1, heat exchange between the solution and the surrounding medium at the moment of freezing is eliminated; 2, the super-cooling correction can be accurately determined; 3, the final temperature remains constant for several minutes; 4, air is drawn through the ether instead of being driven through it, so that ether vapour does not tend to escape into the room; 5, no glass is used except in the thermometer and tap. Insulation is secured by compressed cork casing and the requisite low temperature can be quickly reached.

In the Hortvet method it is necessary to remove the freezing starter from the apparatus before tapping the thermometer.<sup>2</sup>

**Calculation of Freezing-point from the Analytical Data of Milk.** A molecular constant has been deduced which is related to the lactose, sodium chloride, and soluble phosphate (as  $P_2O_5$ ) and to the water content of the milk. It is claimed that the following equation approximately holds:

$$(a) R_s - R_w = 3.48L + 4.52C + 7.14P + K_1$$

where  $R_s$  and  $R_w$  represent the refractive indices of milk serums and of water in degrees Zeiss, and

$$(b) \text{Freezing-point } \Delta = 0.052L + 0.615C + 0.585P + K_2$$

where  $L$  = L g. lactose,  $C$  = C g. chloride as NaCl, and  $P$  = P g. of soluble phosphate as  $P_2O_5$  per 100 gram water.

$K_1$  and  $K_2$  are relatively small quantities representing the contribution of other less important milk constituents. Eliminating  $L$  between the equations gives:

$$66.9\Delta = (R_s - R_w) + 36.6C + 32.0P + K_3$$

The value of  $K_3$  will be relatively small.

The expression  $R_s - R_w + 36.6C + 32.0P$  for a sample of milk is approximately proportional to its freezing-point and is applicable to fresh samples.<sup>3</sup>

This method could probably be applied in other cases, especially with other biological fluids and with other physical constants if the constants were of sufficient importance to determine. The above example is important only as a method in the detection of added water.

**'Mixed' Melting-points.** Impurities generally alter the melting-point of a substance, and in the great majority of cases a lowering is produced. To determine whether two substances of the same melting-point are identical, a convenient method is to mix equal quantities of the two and take a melting-point of the mixture. If the melting-point is not altered the two substances are probably identical.

**Melting-points at High Temperatures.** With substances which melt at temperatures too high to be determined by means of a mercury-in-glass or mercury-in-silica thermometer, the thermo-couple, platinum resistance

<sup>1</sup> *Analyst*, 1933, 58, 686, 260.

<sup>2</sup> *Ibid.*, 1934, 59, 29.

<sup>3</sup> Ryan and Pyne, *Sci. Proc. Roy. Dub. Soc.*, 1934, 21, 11, 113, which paper gives a bibliography of the literature.

thermometer or optical pyrometer (q.v.) is employed. A fair quantity of substance is here required. Precautions may have to be taken to heat the substance in a reducing atmosphere, or other special external conditions may be necessary. The melting-points of iron, nickel, and cobalt have been determined by placing them on a strip of platinum which was heated in an atmosphere of hydrogen by passing an electric current through the strip. Temperatures were determined by an optical pyrometer.

A new type of melting-point apparatus especially suitable for high temperatures has been devised by Mason. It consists of a small metal cylinder bored with two vertical holes for the thermometer and melting-point tube respectively, with a third observation hole at right angles, and having wound round the block a suitable length of insulated resistance wire which can be heated by the passage of an electric current. A convenient size for the cylinder is about 2 inches high with a diameter of 0.75 inch, and it is provided with flanges at top and bottom and a wide flange in the middle through which is bored the observation hole. About 18 yards of No. 26 S.W.G. asbestos-lagged nichrome wire (with a resistance of approximately

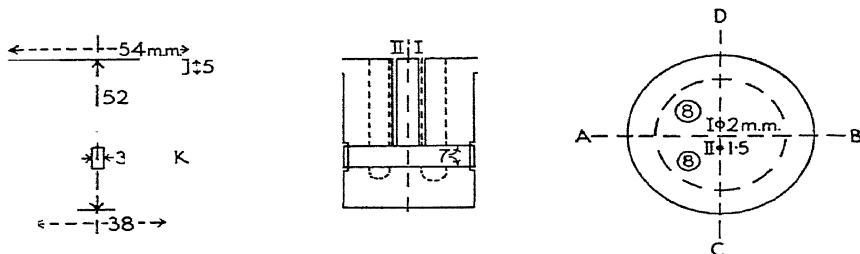


FIG. 22 (VIII)

5.5 ohms per metre) provides a suitable resistance for a 100-volt current; a glass tube is slipped over the whole to stop draughts. The apparatus should be provided with some form of illumination and a small magnifier to observe the substance melting. The current consumption is about 1.0 to 1.3 amps. For use on a 200 or 250-volt circuit an additional variable resistance will be necessary.

Melting-points determined in an apparatus of the type shown in Fig. 19 (VIII) depend on the position of the flame, thermometer, and capillary tube. This is due to stream-line currents with unequal distribution of heat. With high melting-points the errors may be appreciable. When the heating liquid is replaced by a metal block made of a good heat conductor, e.g. copper, these errors are reduced. A modified form of Hermann Thiele's apparatus is described by Berl and Kullmann,<sup>1</sup> and it can be recommended. The dimensions are given in Fig. 22 (VIII). The apparatus consists of a copper block, in cylindrical form, with a projecting ring at the top so as to allow it to hang in the ring of a metal stand. Two holes are bored for two thermometers and two holes for two capillary tubes. The holes are so made that the thermometer and capillary tubes fit closely in them. Otherwise,

<sup>1</sup> *Ber.*, 1927, 60, B. 811-14.

owing to the pressure of excess air (in the apparatus) and to the fact that it is a poor conductor of heat, errors may arise. The two capillary tubes are visible through a tunnel made diametrically through the block and the tunnel may be closed with sheets of mica to avoid variations in temperature due to air-convection currents. The block is covered with asbestos except at the bottom, where it is heated by a small flame, and at the tunnel which allows the capillary tubes to be observed. The two standard thermometers are in the same straight line and they are parallel to the capillary tubes which are placed close to the centre of the block.

In the Eastman Organic Laboratories a modification of this apparatus is used in which illumination of the sample is obtained by a special method. Two pyrex rods are bent and placed at the side of the apparatus so that they transmit light from a lamp to the enclosed portion of the capillary tube. The illuminated area is magnified by means of a lens which aids in observing minor changes, e.g. shrinkage, decomposition, colour change, and so forth.

**The Temperature of Crystallization of Fats.** The temperature at which separation occurs of solid fat from substances such as molten tallow and coco butter is a constant for each fat. Ashmore has devised an apparatus for the precise and rapid determination of this temperature. The Tyndale effect is utilized by projecting a beam of light through a small tube containing the melted fat suitably housed in a darkened chamber; with separation of solid matter, a scattering of light occurs and the tube appears luminous against the darkened background. Fig. 23 (VIII) shows

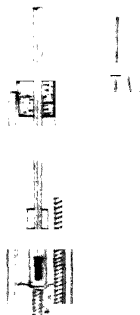


FIG. 23 (VIII)

a diagram of the apparatus.<sup>1</sup> It consists of a glass water-jacketed tube fitted with a cork through which a thermometer passes and a piece of colourless glass rod bent as shown (to convey light from a lamp to the centre of the apparatus). The end of the thermometer is surrounded by a small glass tube ( $1.75 \times 0.375$  inch) closed at one end. This contains the molten fat and is attached to the thermometer with a rubber sleeve. The small tube rests on a seating cut in another cork which is also bored to take the glass rod; in this way the tube sits symmetrically over the end of the glass rod. With the exception of the tip, the glass rod inside the inner jacket is first covered with a layer of polished tinfoil and over this is tightly secured a layer of black paper, this enables sufficient transmission of light through the rod to take place by internal reflection. The illumination is provided by a 60-watt 'day-light' lamp screened from the eyes. A beam of light is led, by internal reflection, along the glass rod and projected upwards through the molten fat. The outside of the water-jacket is covered with a layer of black paper, and in this way a small observation window, indicated by the dotted line in the diagram, is cut so that the appearance of the fat on cooling can be noted. When crystallization begins the solid particles cause a scattering of light and the sides of the tube can be seen fairly outlined. The temperature at which the mass is just uniformly turbid is taken as the crystallization temperature.

<sup>1</sup> Ashmore, *Analyst*, 1934, 59, 515-17.

Independent observers can agree within about  $0.2^{\circ}$  in observing this temperature. The fat must be clear and bright in the molten condition and may require preliminary filtering.

**Setting-point.** When a large quantity of substance is available it is often convenient to determine the setting-point, i.e. the point at which the liquid solidifies. This method is particularly useful in industrial work and in technical analysis where a product is supplied to a specification. A thermometer is immersed in the molten substance, which is slowly cooled until the mercury in the thermometer ceases to fall and rises rapidly to a point where it remains stationary for some time. This latter temperature is the setting-point, and the behaviour of the mercury is due to the heat liberated on the formation of the solid phase.

**Melting-point of Petroleum Jelly.** Certain substances of the nature of petroleum or mineral jelly have no definite melting-point but within a certain range of temperatures change from a viscous to a fluid condition. This point can be conveniently determined by the instrument of Ubbelohde shown in Fig. 24 (VIII). A small quantity of the jelly (about 0.2 gram) is pressed into a small glass cup with a hole in the bottom. This cup fits on to the bulb of a thermometer and on slowly heating the temperature can be noted at which the drops of liquefied petroleum drop away from the cup.

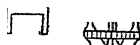


FIG. 24 (VIII)

## SECTION 5: DETERMINATION OF BOILING-POINT

The boiling-point of a liquid is the highest temperature attainable by a liquid, under the pressure of its own vapour, when evaporating with a perfectly free surface and when the heat reaches the surface from without. An apparatus suitable for such a determination is shown in Fig. 25 (VIII). The liquid is placed in a small long-necked flask fitted with a side-tube and usually a condenser. The thermometer is inserted through a one-holed stopper so that its bulb is on a level with the side-tube entrance. Superheating of the liquid and consequent bumping may be prevented by the

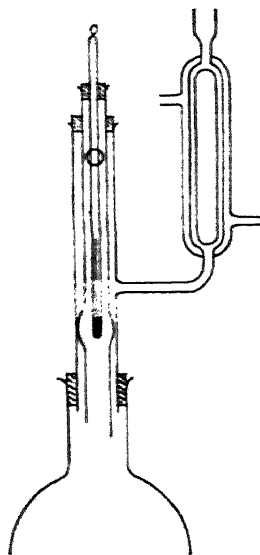


FIG. 25 (VIII)

introduction of a few pieces of porous plate into the flask. The flask is heated with a small Bunsen flame, care being taken not to heat the walls of the flask near the thermometer bulb. When the vapour is seen to distil over regularly and to be dropping from the bulb of the thermometer the temperature of the latter is read. With care this method gives results quite accurate enough for ordinary purposes. A metal shield around the neck of the flask may be used to prevent radiation to the bulb.

Beckmann's boiling-point apparatus, used mainly in the determination of molecular weights, is described in Chapter XIII, S. 2. The other boiling-point methods described in the same chapter may be applied, if necessary, to absolute measurements. In accurate work the method of heating by leading in boiling vapour is to be recommended.

Swietoslawski and Romer<sup>1</sup> describe a new type of boiling-point apparatus (ebulliometer) of simple design and utilizing the Cottrell<sup>2</sup> principle of ejecting the boiling liquid on to the bulb of the thermometer. This was developed to make a differential ebulliometer to measure in an accessible manner the boiling-point and condensation temperatures of liquids. The existence of differences between these temperatures would point to the existence of impurities in a liquid supposed to be pure. Swietoslawski<sup>3</sup> describes the above and other types of boiling-point apparatus in which the simultaneous measurement of boiling-point and condensation temperatures is adapted to

<sup>1</sup> *Bul. Acad. Sc. Polonaise (A)*, 1924, 59.

<sup>2</sup> Cf. Chap. XIII, S. 2.

<sup>3</sup> *Ebulliometry: The Physical Chemistry of Distillation*, Chemical Publishing Co., N.Y., E. and F. N. Spon, London, 1937.

determine the degree of purity of liquid substances and of their azeotropic mixtures.

**Method of Smith and Menzies.** Smith and Menzies<sup>1</sup> have described a method for determining boiling-points; with this method only a small quantity of substance is required and the method may be used for solids as well as liquids. A small bulb, with a wide capillary tube 3–4 cm. long and not less than 1 mm. in width (Fig. 26 (VIII)), is made. The capillary is bent close to the bulb after a small amount of the liquid or pulverized solid has been introduced. It is then attached with thread or asbestos cord to the bulb of a thermometer and fixed in a beaker containing a transparent liquid, fitted with a glass stirrer. Water, sulphuric acid, or melted paraffin wax may be used in the beaker according to the temperature likely to be required. The thermometer being fixed, the bath is heated and stirred. When the boiling-point is reached, the vapour expels all air or other gaseous impurity and bubbles of the vapour of the substance issue in a regular stream. This is allowed to continue for a few moments. When the flame is removed, a fall of a small fraction of a degree in the bath causes a cessation of the bubbles and the same increase causes them again. The reading of the critical temperature is taken and other observations made to obtain constancy of reading.

If the vapour is soluble in the bath liquid, the cessation of the bubbles cannot be noted sharply. Instead, the moment of return of the liquid meniscus to a predetermined point on the capillary is read.

A correction must be introduced to the barometric reading for the depth of immersion of the entrance to the bulb.

For special accuracy, the following precautions must be observed:

(1) Temperature changes near the boiling-point should proceed very slowly and uniform distribution of temperature be secured by continual stirring.

(2) The thermometer must be accurate and the usual corrections made (see Chapter X, SS. 1 and 2).

(3) A capillary less than 1 mm. should not be employed, to avoid any capillary correction (see Chapter XII, S. 5).

For more accurate estimations the bulb should be connected with a manometer and vacuum pump, and the apparatus set in a thermostat. A considerable amount of the liquid should be evaporated to make certain that all the gases dissolved by the liquid under examination or the mercury are removed before determining the actual vapour pressure.

As an example of the need for extreme accuracy in boiling-point deter-

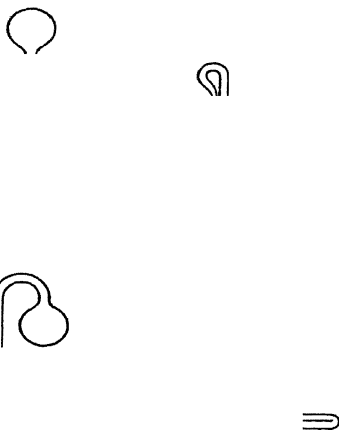


FIG. 26 (VIII)

<sup>1</sup> *J. Amer. Chem. Soc.*, 1910, 30, 897.

mination a reference may be made to a paper by Smith and Wojciechowski<sup>1</sup> on the differences between the boiling-points of dilute aqueous solutions of deuterium oxide and ordinary water in the range from 0.3 to 7 per cent heavy water. The differences were measured in a differential ebulliometer which gave a fractionation equivalent to about one theoretical plate. In the original paper a simple barometric ebulliometer and a differential ebulliometer are described.<sup>2</sup> The original paper should be consulted for further reference on this subject.

**Boiling-point of Acetone-water Mixtures.** The table below shows the relation between the boiling-point of aqueous acetone mixtures and the acetone content of the liquid and the vapour.

Boiling-point of liquid. °C.	Acetone in liquid. Weight per cent.	Acetone in vapour. Weight per cent.	Boiling-point of liquid. °C.	Acetone in liquid. Weight per cent.	Acetone in vapour. Weight per cent.
56.9	100	100	73.3	17.5	86
—	99	99.5	—	15	84.2
57.2	95	97.5	77.16	12.5	81.93
—	90	96.3	81.1	11	79.95
58.3	89	96.18	—	10	78.4
58.9	85.5	95.76	—	9.5	77.6
—	80	95.3	—	8	74.4
60.7	76.5	—	—	7	71.2
60.45	72	—	—	6	67.4
—	70	—	—	5	62.6
61.6	65.5	—	88.7	4.5	59.3
62.4	60.5	—	—	3	47
—	55	—	94.63	2	36
—	50	—	—	1	20.4
64.4	45.5	89.59	—	0.5	11.0
65.3	40.5	87.6	—	0.4	8.93
65.9	36	—	—	0.3	6.85
67	33.5	—	—	0.2	4.78
70.7	24.5	—	99.8	0.1	2.7
—	20	—	—	—	—

For a long list of azeotropic substances (binary mixtures—of minimum and maximum boiling-points and similar tertiary mixtures), and full references, see Young, *Distillation Principles and Processes*, 1922, and *Lecat, La Tension de vapeur des mélanges de liquides, l'Azéotropisme* (Brussels, 1918).

**Boiling-point of Sulphur.** The temperature of equilibrium between liquid sulphur and its vapour at a pressure of one standard atmosphere is defined on the International Temperature Scale as 444.6°, and is a fundamental point for realizing that scale. For substances of such high boiling-point it is usual to use platinum-resistance thermometers. The boiling-point of sulphur has been determined with such a thermometer by Callendar and Griffiths. A simple glass apparatus was used (Fig. 27 (VIII)). A wide glass tube, of the kind employed for Victor Meyer's vapour-density apparatus

<sup>1</sup> *J. Res. Nat. Bur. Stand.*, 1936, 17, 841.

<sup>2</sup> These were made by S. Obojski, glassblower to the Polytechnic Institute, Warsaw.

was cut off to a length of about 40 cm. ; the lower half was padded externally with asbestos. The upper half was left bare to act as a condenser and covered with an asbestos card. The bulb was filled with sulphur and made to stand in a circular hole cut in a piece of asbestos card. The resistance thermometer was inserted and the bulb heated with a Bunsen burner ; the sulphur vapour could be made to rise to any desired height in the tube by regulating the heat supply. The thermometer was protected from loss of heat by conduction and radiation. An asbestos umbrella was made to fit the stem and bound on to it by wire. The constant temperature was then determined by the resistance method.

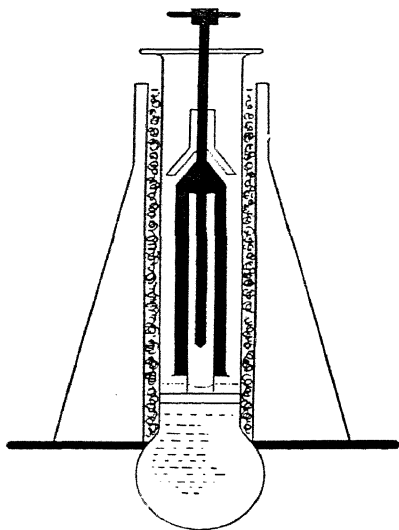


FIG. 27 (VIII)

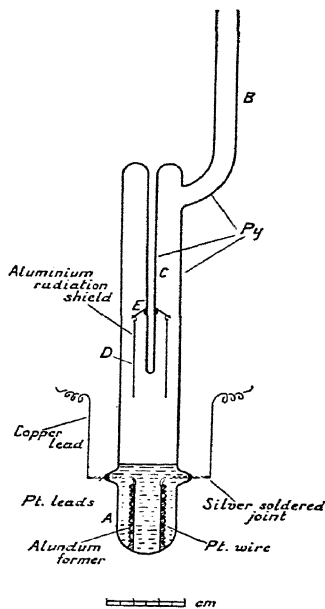


FIG. 28 (VIII)

A sulphur boiling-point apparatus with internal electrical heating suitable for the rapid calibrating of thermo-couples at  $444.6^{\circ}$  has been designed by C. R. Barber.<sup>1</sup>

The boiling tube, A, condenser tube, B, and re-entrant tube, C, for the test couple, were all of pyrex, and the whole was sealed into one unit as shown in Fig. 28 (VIII). It is important that the distance between the bottom of the tube C and the surface of the boiling liquid should be sufficiently great to render impossible splashing of the liquid on to C and consequent disturbance of its temperature. A radiation shield on C is provided to prevent radiation from the latter to the cooler walls of A. This radiation shield took the form of an aluminium cylinder, D, suspended from an aluminium cone, E, held in position

<sup>1</sup> *J. Sci. Instr.*, 1937, 14, 227.



by a slight expansion on C. The gap between the cone and cylinder allows free passage of the sulphur vapour. The heating unit was made up of platinum wire about 0.5 mm. diameter and about 200 cm. long wound on a grooved alundum former. The leads for this unit each consisted of two platinum wires, 0.5 mm. in diameter, twisted together and fused to the ends of the heater wire. These were sealed directly through the walls of the tube so that the whole heater and its leads would be below the level of the liquid sulphur. The platinum leads were silver-soldered to copper wires which were wound once round the sealing-in tubes, thus reducing the possibility of strain at the seals. The whole unit was lagged with asbestos wool. With regard to the pyrex-platinum seals described above, although there is a discrepancy between the coefficients of expansion of pyrex and platinum, no trouble was here experienced on that account.

*Procedure for using Bath.* The following procedure was adopted in operating the bath. A current of 2.5 amps. (20 W.) was passed through the heater for about 15 minutes. This quantity of energy was sufficient to melt the sulphur, a fact that was ascertained by passing a nichrome wire down the condenser tube into the sulphur. Once the sulphur was melted the current was increased to 7 amps. (180 W.), which enabled the boiling-point to be reached in a further 25 minutes and condensation of the vapour to be maintained at a convenient level in the condenser tube. After the sulphur has once been melted and frozen it is important to proceed slowly with the heating on first switching-on so that too violent expansion should not be caused before all the sulphur has melted. Following the above-mentioned procedure, some thirty separate boiling-points were observed by Barber without failure of the apparatus.

Exploration of the re-entrant tube showed that over a distance of 5 cm. variations of more than  $0.1^{\circ}$  did not exist, whilst the temperature value agreed, to  $0.1^{\circ}$ , with that given in the standard sulphur bath used at the National Physical Laboratory.

## SECTION 6: HYDROGENATION

The hydrogenation of unsaturated organic substances with the production of a saturated compound is now a well-established industrial process. The process is utilized on a very extensive scale in the hardening of oils, in the production of edible fats, in the synthesis of methanol, in the winning of volatile products from coal and in the hydrogenation of naphthalene and other compounds to obtain valuable solvents. An enormous literature has arisen in the subject and specialized works must be consulted for the various sections of this wide field. In the present chapter a few applications of hydrogenation on the laboratory scale only will be considered.

In the absence of a catalyst the process, even at high temperatures, is generally very inert. The great activity of nickel as a catalyst in hydrogena-

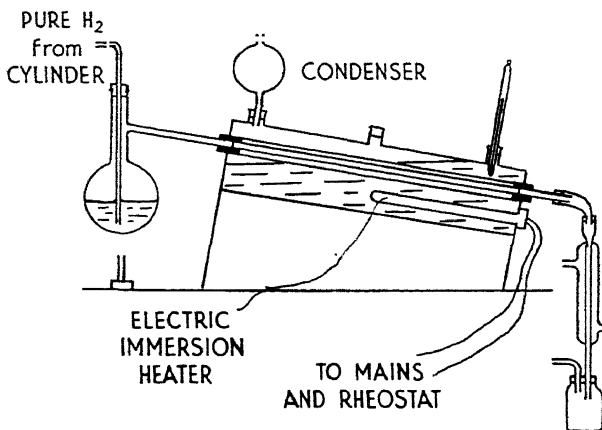


FIG. 29 (VIII)

tion was recognized by Sabatier as early as 1897 and the passage of hydrogen with the vapours of an unsaturated organic compound over heated nickel is known as the Sabatier and Senderen hydrogenation process. This method is still used for work in the vapour phase, especially in laboratory practice and a short description of the method of carrying out this reaction will be given.

The apparatus used by the authors of *Physico-Chemical Methods* has been modelled on the apparatus of Sabatier described in *Catalysis in Organic Chemistry*.<sup>1</sup> A reaction tube 1 metre long with a diameter of 1.5 cm. is employed and this is placed in an oil bath electrically heated. The bath is placed at an angle as shown in Fig. 29 (VIII) to avoid reflux of condensation

<sup>1</sup> Van Nostrand, 1922. Cf. also *Die Katalyse in der Organischen Chemie*, Sabatier and Finkelstein (Leipzig, 1927).

products. The hydrogen may be obtained by the action of zinc on acid, and in this case will require to be purified from sulphuretted hydrogen, arsine, phosphine, &c., first by passing through a hard glass tube containing copper turnings heated to a dull red heat and then through a tube containing lumps of potassium hydroxide very slightly moist on the surface. It is much more convenient, however, to use hydrogen from a cylinder; this is usually electrolytic hydrogen and requires no purification in most cases since there is generally no more than a trace of oxygen present. The cylinder should be provided with a reduction valve and gauges. The first gauge gives the pressure in the cylinder and the second one gives the pressure after passing through the reducing valve. In some cases it may be necessary to use a flow meter when it is desired to measure the amount of hydrogen used.

**Introduction of the Substance to be Hydrogenated.** When the substance to be treated is a gas several obvious ways of mixing with the hydrogen stream suggest themselves. If the substance is a liquid the apparatus shown in the diagram may be used; here the hydrogen bubbles through the liquid contained in the distilling flask on the left and the amount of liquid vaporizing may be controlled according to its volatility by heating or cooling the flask. Another method is to allow the liquid to drop into the heated flask from a burette the top of which passes through the stopper.

Solid substances may generally be vaporized by heating in a well-lagged flask, but in case this is not sufficient they may be placed in a porcelain boat in the reaction tube.

The products of the reaction which are gaseous are collected over the pneumatic trough. Liquids are condensed in a condenser and may be collected, for example, in a Wolff's bottle. Very volatile liquids may need the use of a freezing mixture.

In fitting together the apparatus rubber tubing free from dust and with a smooth inside surface should be used. It is advisable to boil it in alkali before use and when in use to allow it to come in contact with the reactants as little as possible by making junctions of glass or metal with one another, using the tubing merely to hold them together. Reinforced rubber and canvas tubing may be used for pressures up to three atmospheres, but above this it is necessary to use metal unions.

The majority of hydrogenation processes employ one of three systems. In the first system mechanical agitation is employed to obtain an intimate blending of the catalyst and the organic product with hydrogen. The second system employs a circulating process. The organic substance and catalyst are taken from the lower part of the vessel and introduced in an atomized form into the gas space (by means of a pump) at the top of the reaction vessel. The third process is a continuous one and the organic substance passes over the catalyst with a stream of hydrogen.

#### DESCRIPTION OF THE T.R.W. CONTINUOUS HYDROGENATION PROCESS

**Plant.** The industrial scale plant consists of a series of drawn-steel jacketed tubes about 7 feet long and 6 inches in diameter. Each tube holds two catalyst cages, each 3 feet 6 inches long, 6 inches in diameter. These cages are composed of monel metal gauze filled with activated pure nickel turnings. At one end of the series of tubes is placed an oil (i.e. substance to

be hydrogenated) supply vessel fitted with a heating coil, sight and pressure gauges, &c. ; at the other is a separator and cooling coil. The whole plant is self-supporting, being erected on steel framework supports.

**Process.** The first part of the process is the oxidizing of the catalyst cages electrolytically. This is done by immersing them in a bath of dilute sodium carbonate. The cage is placed in the bath and surrounded by a circular nickel sheet ; by making the sheet the cathode and the cage the anode, and passing a current of electricity through the bath the catalyst becomes covered with a thin film of nickel oxide. The current strength required for this purpose is very small, being 40 amps. at 4 volts for each cage ; the period of oxidation is from 24 to 48 hours. The cages are washed and then placed in the reaction tubes. After closing the tubes, superheated steam is admitted to the jackets of the tubes, and hydrogen is passed through the plant at a high temperature. By this means, the nickel oxide is reduced to very active nickel, and, after allowing to cool somewhat, the plant is ready for hydrogenation. Oil is pumped into the supply vessel, where it is pre-heated by means of a heating coil. The oil is forced by hydrogen pressure out of the supply vessel into the main supply pipe, where it meets a current of hydrogen. The oil and hydrogen pass into the top of the first tube and drip through the nickel catalyst to the bottom of the tube ; thence it passes up to the second tube and so through the whole series of tubes.

Having passed through the tubes, the oil arrives at the separator, where it is freed from excess hydrogen gas. The hardened oil is then cooled to a suitable temperature by passing through the cooling coil under the separator.

The Laboratory T.R.W. Hydrogenation Tube <sup>1</sup> is made to the following specifications (Fig. 30 (VIII)) :

*Reaction Tube (B).* 2 feet 6 inches long  $\times$  1 inch internal diameter ; wound for electrical heating, with suitable resistance board and switch. It is fitted with a thermometer pocket and inlet and outlet tubes, high pressure unions, and the whole is tested to 500 lb. per square inch.

*Storage Vessel (A) and Receiver (C).* 8 inches  $\times$  3 inches. Each holds 1,000 ml. The apparatus is fitted with seven 0.125 inch needle valves, one on the hydrogen inlet (H) and the others are marked 1-7 ; sight and pressure gauges, and with all necessary connexions.

*Catalyst Cages.* Two pure nickel cages 1 inch diameter, filled with T.R.W. specially activated pure nickel turnings, and two similar spare cages.

*Cathodes.* Two pure nickel circular sheets, 14 inches long  $\times$  6 inches.

The whole of the above is completely assembled on strong steel framework supports as shown in Fig. 30 (VIII).

A simple and accurate method for quantitative hydrogenation at ordinary temperature and atmospheric pressure with palladium as catalyst is described by Shaefer.<sup>2</sup> This should prove of value in the study of pure compounds of unknown constitution. After good quantitative results had been obtained in the hydrogenation of maleic acid, the method was applied by the designer to  $\alpha$ -pinene, dipentene, diterpene,  $\alpha$ -terpineol, abietic acid, and ethyl abietate.

Made by Messrs. Technical Research Works (T.R.W.), Ltd., Milner Street, London, S.W.

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 1930, 2, 115.

Pinene and dipentene were found to react with almost identical amounts of hydrogen under the experimental conditions imposed.

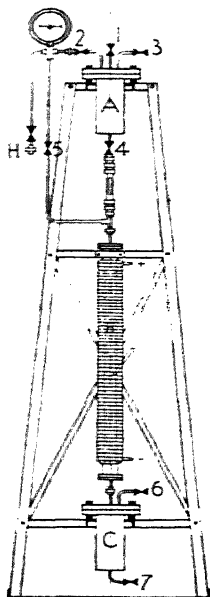


FIG. 30 (VIII)

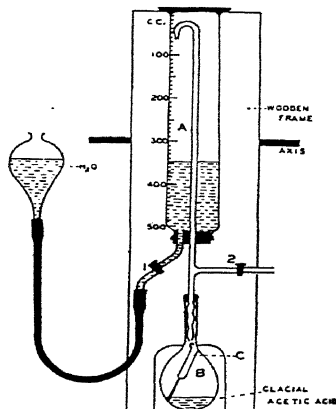


FIG. 31 (VIII)

**Apparatus.** The apparatus is shown in Fig. 31 (VIII). The description and method of working is that given by Shaefer (*loc. cit.*). It consists of an inverted 500 ml. graduated cylinder, A, and a long-neck reaction flask, B, which are connected by a glass tube as indicated and are attached to a wooden frame. The frame is fastened to a horizontal iron axis and shaken mechanically; in this way a very vigorous oscillatory motion is obtained. The upper end of the glass tube inside the cylinder A is bent over and protected from injury by being wrapped with a cloth; the lower end is provided with several bulbs to prevent the glacial acetic acid (which is used as a solvent) in the flask from coming in contact with the rubber stopper and extracting sulphur which would poison the catalyst. The levelling bulb is filled with water saturated with hydrogen. The cylinder A was calibrated while it contained the hydrogen inlet tube. A correction of 2.3 per cent for the volume of the tube was always applied.

**Procedure.** In the reaction flask B are placed 25 ml of glacial acetic acid, a weighed quantity of palladium hydroxide paste<sup>1</sup> (usually 0.5 gram) and a few milligrams of freshly reduced palladium. The palladium is used to start the autocatalytic reduction of the palladium hydroxide. After transferring practically all the water from the cylinder to the levelling bulb

<sup>1</sup> Cf. Piccard and Thomas, *Helv. Chim. Acta*, 1923, 6, 1045.

and closing stopcock, 1, the apparatus is alternately evacuated and filled with hydrogen several times. A gas-washing bottle containing concentrated sodium hydroxide solution is placed in the vacuum line in order to absorb acetic acid vapour and prevent it reaching the vacuum pump.

After the apparatus has been filled with pure hydrogen, stopcock 2 is closed and stopcock 1 is opened. The apparatus, attached rigidly to its wooden frame, is shaken until reduction of the palladium hydroxide is complete, as shown by occasionally measuring the hydrogen in the cylinder, A, at atmospheric pressure. The reaction flask, B, is disconnected from the rest of the apparatus. A weighed sample of the substance to be examined, contained in tube C, is lowered into the flask B by means of a bent wire or hooked glass rod. The apparatus is alternately evacuated and filled with hydrogen several times as before. The volume of hydrogen in the apparatus, the temperature of the cylinder and of the bulb, and the barometric pressure are noted. By shaking the apparatus the thin glass stem at the base of the tube, C, is broken, whereupon the tube falls down and the sample is dissolved in the glacial acetic acid. In every experiment the designer states that the stem broke readily and in only one case did it break prematurely. Readings of volume, temperature, and pressure are made occasionally until the weight of hydrogen in the apparatus becomes constant.

The palladium hydroxide is prepared by the addition of sodium carbonate—avoiding an unnecessary excess—to a solution of palladium chloride. It is pointed out that care must be taken that the palladium chloride solution is free of hydrochloric acid, because palladium hydroxide cannot be precipitated in the presence of much sodium chloride on account of the formation of a soluble complex salt. The precipitate, washed by decantation and filtered by suction, is dried to a stiff paste on a porous plate and preserved in a tightly stoppered bottle. By the ignition of a sample of this paste it was shown to contain 18 per cent of palladium.

For high pressure hydrogenations the apparatus of Adkins and his co-workers<sup>1</sup> may be taken as typical for laboratory work. In the above paper Adkins and Cramer describe the preparation of an active nickel catalyst and the apparatus and technique evolved makes it possible to determine with accuracy the amount of hydrogen absorbed and the rate of reduction. The merits of different solvents are also discussed. In other papers Adkins describes the use of catalysts other than nickel in, for example, the reduction of fatty acid to alcohols by high-pressure catalytic hydrogenation.

In the apparatus used by Adkins the material to be reduced is placed in copper or glass bottles or 'liners' having an internal volume of from 100 to 600 ml. Each liner bears a pinhole in the side half-way between its top and bottom. The effective capacity, i.e. the volume below the pinhole, is 50 to 300 ml. The glass liners are closed by a ground-glass joint and the copper ones by a cap screwing down against a lead gasket. The caps of both types of bottles are designed with a tube extending downward to accommodate a thermocouple well projecting from the head of the bomb into which the liners are inserted. The bombs are made of chrome vanadium steel and the type of bomb closure described by Ernst<sup>2</sup> is employed. One of the bombs had

<sup>1</sup> Cf. *J. Amer. Chem. Soc.*, 1930, 52, 4349, &c.

<sup>2</sup> *Ind. Eng. Chem.*, 1926, 18, 664.

outside dimensions of 26.7 cm. long and 14 cm. diameter, and the other 42 cm. by 11.4 cm. The inside diameter was 6 cm. for both bombs, one having a depth of 16.5 cm. and the other of 31.5 cm. Each bomb bears in the head a thermocouple so designed that the end of a thermocouple could be extended beyond the centre of the reaction chamber. The thermocouples are of No. 20 iron-constantan wire encased in insulation tubes 4 mm. in outside diameter.

Lead gaskets are used in most instances for the bomb closure. Copper gaskets made of copper wire 3 mm. in diameter are employed for pressures above 200 atmospheres. The bomb is placed in a horizontal position in a shaker similar in principle to the one described by Peters and Stanger.<sup>1</sup> The bombs are electrically heated, using 100-volt A.C. current and nichrome wire 0.1 mm. in diameter. Two heating units for each bomb are used, having a resistance of about 27 ohms. The temperature is controlled by a potentiometer controller and recorder.

The valves and connexions used are similar in design to those described

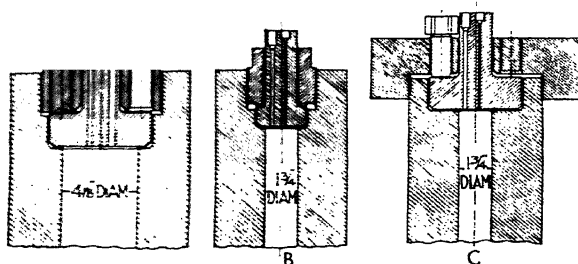


FIG. 32 (VIII)

by Ernst.<sup>2</sup> The tubing is 0.25 inch O.D. by 0.0625 inch I.D. of molybdenum steel. The gauges are of the ordinary commercial type having ranges from 0 to 5,000 or 0 to 10,000 lb. per square inch.

The converter or autoclave heads described by Ernst<sup>3</sup> may be mentioned here. Fig. 32 (VIII) shows three types of cylinder closures. In all three of these cases the retaining bolts are in compression when under load and the bolt circle is as nearly directed over the mean circumference of the gasket as possible, thus reducing the moment in the head. Type A is preferred by the designer, but for experimental work, when the inside diameters of the cylinders are small it cannot always be used. Either B or C, however, is equally satisfactory as to strength and gas tightness. Type B is perhaps a little more difficult to assemble than C, but requires less space and is lighter and somewhat cheaper to fabricate. It should not be used where the nut end would be, across flats, greater than about 4 inches.

Bolts as large as are possible and practicable for the particular apparatus are recommended to be employed, and for the usual cases it would be well to place the minimum size bolt at 1.25 inches.

<sup>1</sup> *Ind. Eng. Chem.*, 1928, 20, 74.

<sup>2</sup> *Ind. Eng. Chem.*, 1926, 18, 664.

<sup>3</sup> *Loc. cit.*

In A, the joint is made by placing the head in position on the gasket in the end of the cylinder, the retaining ring with interrupted threads is dropped into place, and given sufficient circumferential turn to engage the threads for their full length. The bolts are then screwed down until the joints are made tight. Type B is similar, except that there is but one bolt, which is also the retaining ring. In this case the threads are not interrupted. In C, where the diameter of the tube is not sufficient to permit of enough bolts to hold the pressure, as in A, the threads of the retaining ring of the cap type engage threads cut into the outer periphery of the cylinder. The bolts are then tightened in a manner similar to those of A.

The gasket is of copper, silver, or some other relatively soft metal which will actually flow under the pressure of the bolts, thus filling the small 'V' groove cut alike into both the seat in the cylinder and in the head. A method of figuring this gasket is described by Ernst, Reed, and Edwards.<sup>1</sup>

The shaking apparatus and a small high-pressure autoclave described by Peters and Stanger<sup>2</sup> may also be given here. The size of this apparatus may be varied within rather wide limits, but the one illustrated is designed to handle about 1,200 ml. of liquid. The shell is made of two pieces of 3-inch, double-extra-hydraulic steel pipe, 18 inches long; two 3-inch double-extra-heavy steep caps, and a tee of the same material. The two pieces of pipe are screwed into the tee, T, and one end is closed by a cap, G. It is suggested by the designers that these three joints be welded. The open end of the pipe is machined so that it presents a perfectly true face. In the centre of this face an annular groove, G, 0.0625 inch deep, is turned. A steel disc, D, the same diameter as the pipe, has two similar grooves cut in one face, so that when it is placed against the end of the shell, A, the two grooves will span the groove in the face of the pipe. Lead gaskets, R, with annular ridges to fit into these grooves are cast from a special mould. The method of assembling these parts is shown in the enlarged sectional drawing which also shows the method of mounting for agitation (Fig. 33 (VIII)). It is advisable to cover the gasket and threads with a graphite pipe-joint compound to insure a tight closure and ease of opening. With this apparatus hydrogen it is stated by the designers has been held at 1,500 lb. pressure for 2 weeks with absolutely no leakage.

The method of connecting the copper tube to the shell may vary according to operating conditions. In the apparatus shown there is a Tobin bronze tee, M, with a male thread which fits into the iron tee, T. A standard hydrogen valve, V, is fitted into this bronze tee and is attached to a pigtail connexion through which the pressure may be released or the apparatus evacuated before introducing the hydrogen. The copper tube is connected to M by a hydrogen nut, N, and a short nipple. This nipple may be replaced by a valve if it is desired to maintain pressure in the apparatus when the hydrogen cylinder is removed. These valves are unsatisfactory at temperatures above 100°, but if they are raised 10 or 12 inches from the shell by means of a short length of double-extra-heavy pipe, a working temperature of 250° may be maintained without harm. It could also be arranged to place the valves near the hydrogen cylinder and connect the copper tube to T by means of a short nipple. The iron tee is used only to give wall thickness sufficient

<sup>1</sup> *Ind. Eng. Chem.*, 1925, 17, 775.

<sup>2</sup> *Ibid.*, 1928, 20, 74.



for connecting the brass tee, thermocouple leads, &c., by means of threads. If larger pipe is used, the wall thickness may be sufficient to warrant drilling and tapping the pipe itself, thus eliminating the tee.

The copper tube on this particular machine is 15 feet long, which includes three bends around the shaft. A special tee is placed in the tube from which a lead goes to a recording pressure gauge. The designers consider it an open question as to how long these tubes would stand up under the bending to which they are subjected, but it was stated four of them had been in operation for over 400 hours and there was no sign of deterioration.

Heating is accomplished by eight 12-inch space heaters, H, mounted around the shell on strap-iron supports, S. By means of a three-heat switch (not shown in the drawing) wattages of 1,760, 880, and 440 could be obtained. Low heat will maintain a temperature of 130–160°. The insulation, I, is of asbestos cement protected by a sheet iron covering, P. The upper half of the

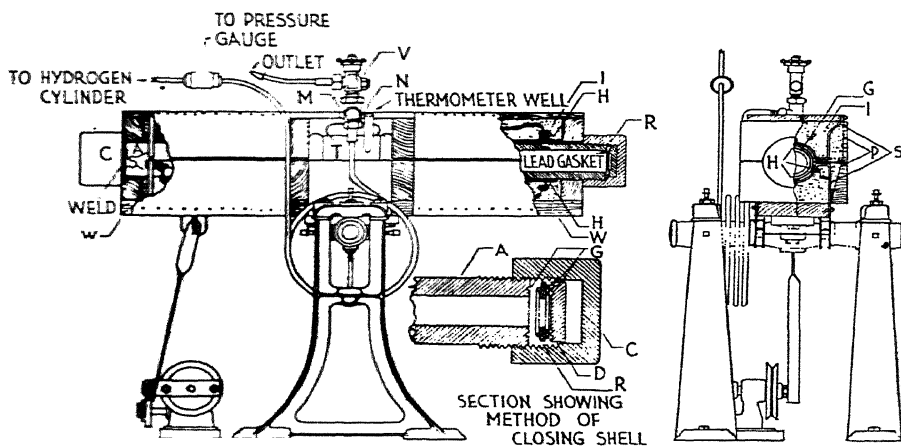


FIG. 33 (VIII)

insulation, containing two of the space heaters, is built so that it may be removed, thus enabling the shell to be taken out for examination or repair. Connection between the upper and lower heaters is made by a flexible connexion and plug.

The apparatus is operated by a motor-driven reducing gear. The crank makes 12 revolutions per minute and is constructed from 0.5-inch strap iron, a 5-inch pulley, a pillow block, and cap screws. The method of assembly is shown in the drawing. Two rockers of the size shown are driven from one of these gears, which indicates that the power requirement is very small.

The base, W, on which the shell and heaters rest is mounted by means of a flat box on a shaft, which in turn is supported by ordinary hangers. In an earlier type of autoclave used by the designers the hydrogen cylinder was directly attached to the under side of this base and was connected by a rigid tube to the shell, doing away with the long flexible tube, which is rather expensive. In this early form the hangers were mounted on swivel casters

and the apparatus, hydrogen tank and all, could be moved readily from place to place. In the drawing a thermometer well is shown welded to the side of the tee. If the apparatus is to be used at fairly constant temperatures, this method of measurement will be moderately satisfactory, but if the exact temperature of the reactants is required, and particularly if the apparatus is subjected to sudden temperature changes, a thermocouple was suggested to be placed inside the shell with the leads coming through the tee. Directions for running these leads through the shell are given by Ernst.<sup>1</sup>

In working with high pressures, make-shift apparatus is in general to be avoided but for pressures such as described in the above paper the designer believed that the dictates of safety are fully satisfied by the material described.

The necessity for the provision of relief valves or of 'blow-outs' in high-pressure apparatus should, of course, be noted and for those unaccustomed to the work the securing of a reliable apparatus is probably the best procedure. The Parr high-pressure apparatus<sup>2</sup> as marketed by Messrs. W. Edwards & Co., Allendale Works, London, may be described.

#### THE PARR HYDROGENATION APPARATUS MODEL B3C<sup>3</sup>

This is of use for catalytic reductions requiring heat, pressure, and agitation in the study of the hydrogenation and condensation characteristics of organic compounds. It is a development of the original of Adkins and incorporates many refinements conducive to safety, convenience of operation, ease of maintenance, and reliability. A monograph by Dr. Adkins, entitled 'Hydrogenation and Hydrogenolysis over Copper-Chromium-Oxide and Nickel Catalysts', is published by the University of Wisconsin Press.

*Description.* The apparatus consists of a bomb, heater, and oscillation mechanism (Fig. 34 (VIII)). The temperature range is from atmospheric to 400°, and the pressure range is from atmospheric to 300 atm. The cubic charging capacity is 200 ml. without the glass liner, or 150 ml. when the liner is used. The internal volume of the bomb is approximately 480 ml.

The bomb (Fig. 35 (VIII)) is constructed of alloy steel throughout. The cylinder is of 18-8 stainless steel, with 0.75-inch wall and 1-inch bottom.

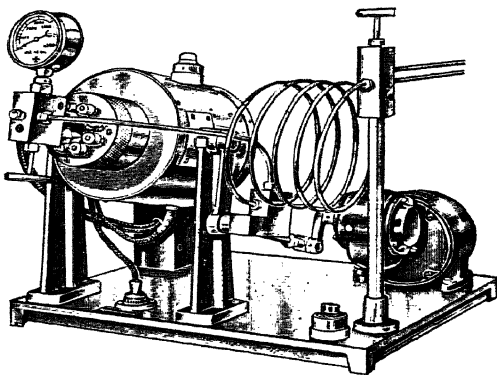


FIG. 34 (VIII)

<sup>1</sup> *Ind. Eng. Chem.*, 1926, 18, 664; *Chem. Met. Eng.*, 1927, 341, 51.

<sup>2</sup> Parr Instrument Co., Illinois, U.S.A.

<sup>3</sup> Made by the Parr Instrument Co., Moline, Illinois, U.S.A. This apparatus is also obtainable from Messrs. W. Edwards & Co., Allendale Works, London, S.E.

The inside diameter is 2.5 inches and the depth 6 inches. A thermocouple well is located in the wall. The bomb head is made gas-tight by a soft copper gasket of diamond section. This presses into a groove, causing it to adhere to the head. It can be easily pried off for replacement. A tube runs from the gas inlet under the head, to a point within the bomb where submergence does not occur during operation. The Pyrex-brand glass liner (Fig. 36 (VIII)) has a close-fitting cover with a ground joint,

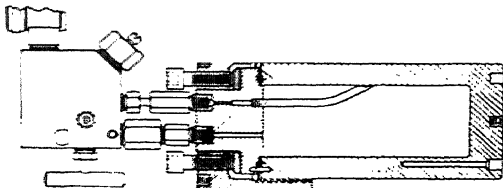


FIG. 35 (VIII)

lapped in place to gasoline tightness. A steel spring-clip holds the cover down and also serves as a handle. A small hole in the side of the liner is located like the 'breather' tube and serves the same purpose. The liner is charged before insertion in the bomb, and withdrawn as a unit after the run. The bomb head is equipped with a safety plug containing a rupturable disc which will burst at a pressure of about 6,000 lb. per square inch, blowing the contents of the bomb downward through an aperture in the gauge block. The screw cap which effects the closure between head and cylinder, is made of S.A.E. No. 3140 chromium-nickel steel, heat treated. It has buttress-type threads for maximum strength. Eight cap screws run downward through it. They are of chrome-molybdenum steel, with socket heads. They exert a uniformly distributed compressive force on the copper gasket, through a thick hardened steel washer which is interposed between cap screws and bomb head. The weight of the assembled bomb is approximately 30 lb., not including gauge-block and gauge.

The gauge block is made of cold rolled open-hearth steel, 1.25 × 2.5 × 4 inches. It is mounted on the bomb head by attachment to the safety plug with a set screw. The gas connexion from block to bomb head is through a short, straight length of chrome-molybdenum steel tubing, 0.25 inch diameter × 0.0625 inch bore, case-hardened. The gauge-block valve controls the gas inlet without interrupting the flux between gauge and bomb. A pocket or trap is located in the channel between gauge and bomb, to be filled with granular soda-lime if weak acid vapours are to be present, thus avoiding corrosion of the gauge.

The gauge is of a special type, with steel Bourdon tube having solderless joints at socket and tip. It is graduated from 0 to 6,000 lb. per square inch, and is tested for accuracy from 1,000 to 4,000. The 4.5 inch dial is divided in units of 1,000 lb., 200 lb., and 40 lb., which permit estimation to the nearest 10 lb.

The gauge-block inlet is connected to the junction block through a swivel tube of 0.25 inch × 0.0625 inch chrome-molybdenum steel. The L-shaped

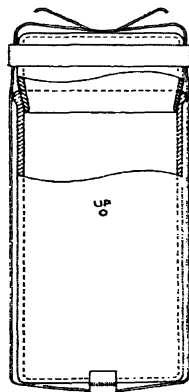


FIG. 36 (VIII)

junction block is hung at the end of a rocker arm, in a position such that its inlet is at the end of the helix formed by the spring tube. The latter, also of 0.25 inch  $\times$  0.0625 inch chrome-molybdenum steel, has its stationary end connected to a booster valve block, at the top of a rigid steel column. The spring-tube connection runs straight through the booster block to the lower supply tube. The upper supply tube connects with the spring tube through the booster valve in the top of the block.

The heater shell (Fig. 37 (VIII)) is a heavy steel casing 10 inches in diameter with asbestos board ends. Solidly mounted within it, and insulated with mineral wool, is the heating element, into which the bomb is fitted. The winding has three taps manually controlled by a rotary switch, for operation at 375, 750 or 1,500 watts. The line from the switch runs directly to a relay of the latch type, which is wired so that the circuit through the coils is closed only during the moment of actuation. Relay operation is obtained through a 3-wire circuit connected to a thermoregulator, which is mounted on the rear of the heater. It is adjustable in steps of about  $10^\circ$ , by means of a knurled nut. This entire system is fed from a single electrical outlet, located on the base plate under the heater, in parallel with the motor, which is controlled independently of the heater by a switch on the right. Power for the complete apparatus is obtained through a single 2-wire extension cord, entering the rear of the base plate. The base is 24 inches long and 20 inches wide.

The  $\frac{1}{8}$  h.p. motor has a worm geared head of a very rugged type. The shaft rotates at 36 r.p.m., imparting a rocking motion to the heater and bomb through a linkage consisting of crank, connexion rod and rocker arm, with a total arc of oscillation of  $45^\circ$ . The rocker arm is attached to the heater trunnion. The mean position of the bomb may be altered to any point between horizontal and vertical. The normal setting is horizontal.

Extending rearward from the booster valve block are two hydrogen supply tubes of soft copper, 0.1875 inch diameter  $\times$  0.0625 inch bore  $\times$  7 feet long. Both tubes are fitted at their outer ends with type VB needle valves for attachment to a pair of hydrogen cylinders. The booster valve and gauge-valve block have type VB packing glands and hardened stainless steel needles. All tube-connexions are of the metallic line-contact type without gaskets.

A copper-constantan thermocouple is provided with the apparatus, but no potentiometer is included. A complete set of wrenches, bomb bench plate, extra gaskets, extra blow-out discs, and other necessary fittings are standard equipment.

The stainless steel construction of the bomb permits operation with strong alkalis or weak acids, which would ruin a carbon-steel bomb. Also, deterioration does not occur while not in use. Admittedly the structural

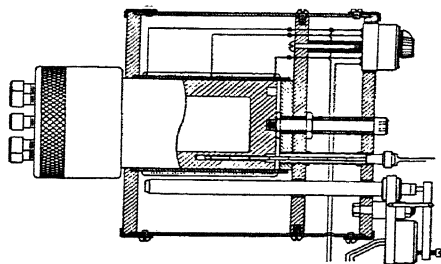


FIG. 37 (VIII)

strength is below that of certain high-tensile steels. However, the bomb has a calculated safety factor of 5, at 6,000 lb. pressure and 400°, at which point the safety disc will rupture. Therefore, the risk of explosion is remote.

The safety plug contains an orifice ring which may be varied in size to obtain different bursting pressures. The standard ring is 0.28125 inch I.D. for 6,000 lbs. maximum. An 0.34375 inch ring can be supplied for student work, to burst at 4,500, also a 0.25 inch ring for special work, to burst at 8,000. The standard disc is interchangeable with these rings. It is of monel metal, 0.5 inch diameter  $\times$  0.015 inch thick.

The period of service obtainable from a single copper head-gasket has been extended by locating the head in a fixed position, by means of a dowel pin. Thus the contacting surfaces are identical each time the bomb is closed, and repeated compression to the point of cold-flow of the copper is not required in obtaining perfect seals. This also saves wear and tear on the cap screws. These have socket-type heads, which eliminate stripped threads as the wrench will slip in the head before a thread will break.

In practice the glass liner is so convenient that it is usually employed continually. It is superior to a copper liner in all respects, excepting ruggedness and thermal conductivity.

The temperature of the charge is determined by observing the environment temperature, by means of a thermocouple inserted in the bomb wall through the rear of the heater. The mass of the bomb is so relatively great that the temperature of the charge varies practically in unison with that of the bomb. Therefore, the temperature of the inner bomb-wall represents a true average temperature of the material in the bomb cavity. Lag, and other complications inherent with a centrally located thermocouple tube, are avoided.

The gauge has a 'safety' back and a pyralin crystal. There can be no damage from ruptured case and shattered glass, if an internal leak should suddenly occur.

In removing the bomb from the heater, only two gas connexions require loosening, namely, those on the swivel tube. This is then swung to the right, two handles are inserted in the bomb cap, and the hot bomb is withdrawn at once for cooling in water. The bomb should not be blown off until cold, thus delays in handling are avoided. Immediately after a run, the bomb may be withdrawn, quenched, blown off, and made ready for a new run.

No sharp bends are present in any of the tubing. The flexible gas connexion is through the spring tube, which is coiled in a 9-inch helix. In operation, no direct bending forces are applied. The helix is placed only in torsion by the rocking of the heater, with the result that stress concentrations do not occur at any point in the coil. The probability of fatigue failure is, therefore, remote, and the life of the coil may be considered as practically unlimited.

Two hydrogen supply lines are provided. A fresh cylinder may be kept on the upper line for obtaining maximum pressures, while preliminary charging is done from a partially depleted cylinder on the lower line.

Economy of gas is thus effected, without losing the availability of high pressures. Also, a hydraulic booster may be used on the upper line, for obtaining pressures above the 125 atm. normally available from a fresh cylinder. However, pressures of 200 atm. and above are usually obtained by charging the cold bomb to 125 atm. and then raising the temperature to 220°, &c.

All valves are designed for the handling of compressed gases. Their packing glands may be made exceedingly tight and proof against leakage, without spoiling their free action and precise control.

The heating element is wound on a copper cylinder, bored to a sliding fit on the bomb. Thermal conductivity is excellent, and the heavy bomb is well supported. The assembly is arranged for easy replacement, and spare elements are interchangeable. Operation of the heater is independent of the motor. The bomb may be rocked with the heat turned off, and vice versa, or both oscillation and heating may be carried on simultaneously. Automatic control is continuous on either low, medium or high heat. The sensitive thermoregulator will hold the bomb temperature within 3° of the setting, and it will not cut in and out from vibration. The heat input is rapid, permitting the temperature of the bomb to be raised at a rate of about 10° per minute in the low range and 8° in the high range.

The apparatus has been designed with all possible care for safe operation. Nevertheless it must be stated that hydrogen, or any other gas at pressures of several thousand pounds per square inch, is potentially capable of great destruction. Inasmuch as operating technique and maintenance of the apparatus are beyond the makers' control, they are not responsible for accidents.

*Utilization.* In the reduction of numerous organic compounds, simultaneous reactions occur. These 'side-reactions' may often be controlled by means of the temperature, pressure, reaction medium, or character of the catalyst, which increase the yield of the product desired. Decided advantages have been shown in the use of pressures up to 150 atm. as compared with pressures below 5 atm., especially in the use of nickel as a catalyst. The apparatus provides pressures up to 200 atm. at 220° in normal operation, and higher pressures can be obtained.

In carrying out reductions, the progress of the reaction is observed by noting the decrease of pressure in the system. The volume of hydrogen equivalent to given changes in pressure, depends upon the volume of the bomb and its temperature. However, the necessary data are usually obtained by standardizing the bomb with some compound which is reduced quantitatively without side reactions, such as toluene or acetone.

The relationship of pressure to rate of catalysis by nickel, is subject to considerable difference among various types of compounds. For example, it is impracticable to reduce aniline at 30 atm., but increased pressures greatly increase the rate of hydrogenation. Thus in a thorough investigation of rates of catalysis, it is essential that a wide range of pressures be available.

The extent of the field of application for an apparatus of this kind cannot be well defined. Originally used for studying catalysis by nickel, it is equally adapted to other catalysts. The list of organic compounds

subject to investigation through catalytic reduction extends into the hundreds.

For apparatus designed for the destructive hydrogenation of coal or oil the reader is referred to those described from time to time in the reports of the Fuel Research Board.

*See also Chapter IX. High Pressure Technique.*

## SECTION 7 : PHOTOGRAPHY

**Photography** has been of great assistance in physico-chemical work, sometimes, as in X-ray, spectroscopy, microscopy, spark discharge, radio-activity, etc., allowing observations to be made which would have been otherwise impossible, and more generally shortening and improving in accuracy those which would else have been tedious and difficult.

The essential parts of a photographic camera are :

(i) The lens, which forms an image of the subject to be photographed on the sensitive surface.

(ii) A sensitive surface—plate, film or paper—to receive and fix the image.

(iii) A supporting framework, usually including an extensible bellows body, to hold lens and plate and keep them in their correct relative positions, and also to prevent extraneous light falling upon the plate.

*Details.* The lens is carried in an upright front, which also holds an adjustable diaphragm or stop to regulate the amount of light entering the camera through the lens, and usually a shutter to govern the duration of the exposure. The sensitive plate is carried in an upright back. Front and back are connected by a rigid baseboard which may be either fixed or extensible and a tunnel (to exclude all light) which may be fixed or extensible (bellows form). Other features are a focusing screen, some form of plate-changing device, and in some instruments a swing back and a rising front. This description refers to a type of camera most likely to be found in use in laboratories and not to cameras generally.

The lenses used in photography are seldom simple but are built up of several kinds of glass to correct various aberrations, spherical and chromatic, which are prominent in single lenses. Photographic lenses include a number of special types developed for particular qualities, e.g. very large aperture, great covering power, unusually short camera extension (telephoto lenses) or the separate use of components as long-focus lenses. For general laboratory use the most useful type is the medium-aperture anastigmat ( $f/6.3$  to  $f/6.8$ ), though some of the old rapid rectilinears ( $f/8$ ) will still give very good service. For accurate reproduction work, as for example in the photographic reduction of line diagrams in the making of graticule scales, a process lens is desirable, on account of the specially fine correction possible in these lenses by virtue of their small aperture and narrow angle of covering power : and for measurements of brightness distribution from photographs, when freedom from flare spots or image degradation is all-important, the best is a simple lens of the old landscape type.

Diaphragms or stops are usually designated in terms of the focal length of the lens system. For instance,  $f/8$  means a stop whose diameter is



one-eighth of the focal length of the lens. The divisor is generally termed the  $f$  number of the stop. The larger the  $f$  value, therefore, the smaller the aperture: the area of the aperture, and therefore the amount of light which reaches the plate, being inversely proportional to the square of the  $f$  value. The following table gives the relative values of exposures for the different stops in common use, when that for  $f/8$  is taken as unity.

	$f/11$	$f/16$	$f/22$	$f/32$	$f/44$	$f/64$
$\frac{1}{4}$	2	4	8	16	32	64

Stops larger than  $f/3.5$  are used in special cameras, and in recent years more and more ordinary cameras have stops as large as  $f/4$ . It is sometimes advantageous to use a fairly small stop, e.g.  $f/22$  or  $f/32$ , as the sharpness of the image is thereby improved. It is doubtful whether the statement, made as simply as this, is advisable. Actually, the resolution obtained is best at maximum aperture: the covering power is improved up to a certain point by stopping down: depth of field increases with stopping down: but diffraction effects at very small apertures are liable to interfere with resolution. Thus it is, on the whole, best to recommend moderate stopping down only, unless either the need for great depth of field or an extended exposure time gives a special reason for a small aperture.

The sensitive plate formerly consisted of a glass support on which is spread a gelatine emulsion containing suspended particles of silver bromide. It is not altogether correct to refer exclusively to 'plates' and 'glass support' at this point: films with cellulose nitrate or cellulose acetate ('Safety') base are used fairly largely in scientific work, for which purpose they have the definite advantages of freedom from breakage and ease of storing in negative form. When light falls upon the plate some change occurs in this salt, although it is apparently unaltered, which renders it more easily reducible to metallic silver by certain reducing agents (such as alkaline pyrogallol acid) known as 'developers'. The intensity of the silver deposit produced at any point of the plate by this treatment is within certain limits, provided that a reasonably correct exposure is given, proportional to the intensity of the light which has reached it, and a reversed image in metallic silver is thus obtained whose densest parts correspond to the brightest parts of the object photographed, and *vice versa*. This image is called a 'negative'. After development the residual unaltered silver bromide must be removed to prevent any further changes. This is accomplished by treating the plate with a solution of sodium thiosulphate ('hypo') and is known as 'fixing'. The final treatment consists in washing the plate free from hypo and allowing it to dry. It is then used for the production of a 'positive' image by 'printing'.

**Types of Negative Material.**<sup>1</sup> Sensitive plates and films available commercially are of various types having widely different qualities and intended in some cases for very specific purposes. Those varieties which are of the

<sup>1</sup> For information on negative materials and useful criticism thanks are due to E. R. Davies, Superintendent, Kodak Research Laboratory, London.

highest sensitiveness to light are of comparatively little use in laboratory work, in which fine detail is usually more important than the shortest possible exposure: in all sensitive materials containing silver salts the granular quality of the developed silver image tends to be more marked the greater the sensitiveness of the emulsion. Hence for images of fine definition it is preferable to use plates or films of medium-speed or 'Commercial' grade. These materials also have the advantage that they are easier to manipulate in the darkroom, since brighter illumination may be used, and that they give negatives of good contrast with conveniently short times of development. When particular jobs call for the finest possible definition or the greatest possible increase in contrast, a slow material or one of the Process varieties should be chosen.

Silver bromide emulsion is sensitive mainly to the blue, blue-violet, and near ultra-violet; but by the introduction of certain dyes in very small amounts to the emulsion the sensitiveness to certain rays is increased. Orthochromatic materials are those in which the sensitiveness has thus been extended to the blue-green, green, and yellow. When the sensitization is extended still further, into the orange and red, so that the material is sensitive to all the colours of the spectrum, the material is said to be panchromatic. Such plates are supplied by various manufacturers ready for use: they require manipulation in total darkness or by very dim safelight, or else must receive, before development, a preliminary treatment in a bath of desensitising dye. The sensitiveness may be extended right into the infra-red by means of other dyes, notably kryptocyanine (to 1,000  $m\mu$ ), neocyanine (to 1,160  $m\mu$ ) or with recently discovered carbocyanine dyes even beyond 1,300  $m\mu$ .

In addition to the ordinary commercial varieties of plates and films the leading manufacturers produce a number of special materials for scientific purposes, having special contrast characteristics, special ranges of colour sensitivity, or these two in combination. Full information on these materials is contained in the booklets *Photographic Plates for Use in Spectroscopy and Astronomy* (Eastman Kodak Co.) and *Photography as an Aid to Scientific Work* (Ilford).

Whilst the use of colour-sensitive materials is naturally an essential part of the technique of photographing coloured objects in such a way that the black-and-white tones of the photograph accord with the visual brightnesses of the colours, this problem also demands a knowledge of the use and choice of photographic light-filters. Even in the most highly sensitive materials the sensitivity of blue rays is still disproportionately great in comparison with that of other colours and it is therefore necessary, for correct colour rendering, to use a filter which will allow only a diminished amount of blue light to reach the film, whilst passing the maximum amount of light of the colour to which the emulsion is less sensitive. For these reasons yellow light-filters of different depths allow a complete control of colour rendering with orthochromatic materials, whilst in the case of panchromatic materials the appropriate filters may be either yellow, yellow-green or green in accordance with the particular sensitizing of the emulsion and the degree of colour correction which is necessary. In certain cases, however, the most useful record of the given subject may be one in which the rendering of colours is

distorted so as to produce an untrue degree of contrast between two totally different colours which may be approximately alike in visual brightness and thus normally appear like as the same tone of monochrome. This possibility of control is effected by the use of exceptionally dense filters, usually yellow to orange or red in colour, which are known as contrast filters. Any filter transmits only a reduced amount of light, so that its use involves an increase of exposure; this increase is not a constant for any filter but depends on the colour sensitiveness of the material; however, the manufacturers will always supply exposure factors for the filters recommended for use with particular materials, for all the principal forms of illumination. For further references on the subject see Neblette, *Photography: Its Principles and Practice* (London, 2nd edition, 1931); Kodak, Ltd., *The Photography of Coloured Objects* (London, 1934); and for the subject of photography in natural colours, see Newens, *The Technique of Colour Photography* (London, 1936).

With all photographic materials the sharpness of the image suffers because the image tends to spread, either by scatter of the light in the emulsion or by the penetration of light through the emulsion and its reflection back from the support. To eliminate this latter fault, which is known as halation, plates or films should always be used 'backed'—i.e. with an absorbing dye backing—when the finest reproduction of detail is necessary.

**The Taking of a Photograph. Manipulative Details.** As an example, suppose it is desired to make a reduced copy of a diagram. The procedure may be conveniently considered in the following steps: (i) Erection of camera and focusing; (ii) loading the slide; (iii) exposure; (iv) development; (v) fixation; (vi) washing; (vii) preparation of 'positive'.

(i) The object to be photographed (a diagram) is placed in a good uniform light, e.g. pinned to a wall well illuminated by daylight, or, more usually, by two electric bulbs placed one at each side of the object and about a foot in front of it, and so shaded as to prevent any direct light from them reaching the camera. The camera is placed with the lens pointing directly to the centre of the object to be photographed and about two feet away from it, and the bellows is extended by means of the focusing screws until the image is seen sharply defined on the ground-glass screen at the back of the camera. The distance of the camera from the object and the extension of the bellows are altered until the image on the ground glass is the size required. In many cameras permanently set up for copying work these adjustments are facilitated by having the front and back of the camera sliding between battens or guides on a baseboard attached to the stand for holding the object, and graduated to indicate the correct positions of back and front for different degrees of reduction.

(ii) Loading the dark slide with the plate must be carried out in a dark-room in which the only illumination is a very dim green light. A red light is not safe with panchromatic plates. As the plates are always packed in pairs, face to face, there is no difficulty in inserting them in the slide with the sensitive side outermost. In case of doubt the clear reflection of the lamp in the glass side of the plate will serve to differentiate it from the film side. Films are notched at one corner so as to give an infallible guide by feel for identifying the sensitive side.

The slide may now be placed in position in the camera, replacing the

ground-glass focusing screen. If the cap is now placed on the lens the slide may be opened and is ready for exposure.

(iii) The correct *exposure* depends on a number of factors, such as the intensity of the illumination, the sensitiveness of the plate, the stop used, the subject, the distance of the subject from the camera (or the degree of reduction). It is true that many modern materials have a very great latitude, so great that it is possible to obtain good prints even when the exposure has been several hundred times the minimum tolerable exposure: yet in practice it is always very desirable indeed to give an exposure that is approximately correct, since the subsequent printing is then as easy as possible. If daylight is the illuminant used its intensity may be estimated by a Watkins B meter, and a very good estimate of the correct exposure obtained by consideration of this result and the other factors. Modern practice tends greatly to favour the use of optical exposure meters working on the extinction principle, or still, more exposure meters incorporating rectifier cells. In general, however, where the same camera and illumination, &c., are in use it is best to determine the correct exposure by trial for a definite stop, brand of plate, and degree of reduction. This may be done by exposing the whole plate for a time (say 5 seconds) likely to prove insufficient, then closing the slide partly so as to exclude a strip of the plate from further action, and allowing a second 5 seconds' exposure, then closing the slide a little more, and allowing 10 seconds, and so on, doubling the exposure each time. In this way the plate is made up of a series of strips which have received 5, 10, 20, 40, 80, 160, &c., seconds' exposure respectively. Subsequent development will show which strip gives the best result, and the corresponding exposure can be noted and used as a basis for subsequent exposures, using other stops and reductions. The effect on the exposure of varying the stop has already been noted. If other conditions are the same the exposure needed will vary directly with the degree of reduction. This is true only for small ratios of reduction or enlargement say up to 10, and then only approximately. Taking equal size copying as unity, the factor for reduction to  $\frac{1}{16}$  is 0.3 and for a  $\times 10$  enlargement 30.25. Thus a full-size copy will require twice the exposure necessary for a half-size.

(iv) *Development* must be carried out in a safe red or yellow-red light, but this statement requires qualification. The dark room light permissible varies with the speed and colour sensitiveness of the material. A very slow material would allow of a yellow-red light; an orthochromatic material a red light, but a panchromatic material would allow only an extremely dim green safelight at most. The following developer is easily prepared and is suitable for most classes of work:

Solution A.	Sodium sulphite cryst.	120 grams	} make up to 400 ml. with water.
	Pyrogalllic acid	20 grams	
	Potass. metabisulphite	5 grams	

Solution B. Sodium carbonate cryst. 80 grams. Make up to 400 ml. with water.

These solutions are kept separate. The developer is made up, when required, by taking 10 ml. of solution A, 10 ml. of solution B, and 60 ml. water. These are mixed in a half-plate (or convenient) dish, and the plate

is taken out of the slide, immersed, film side up, rapidly and evenly, rocked gently for about 4 minutes, and then removed and rinsed under the tap for about 1-2½ minutes. The time of development is of vital importance in controlling the contrast obtained in the negative, because throughout the period of active development—i.e. until the process comes to an end owing to the complete development of the image—the contrast is increasing. The rate of accumulation of density and contrast is influenced markedly by the temperature, and furthermore, different materials may develop at altogether different rates. A number of proprietary developers are available, however, which minimize the difficulty of judging correct development by means of tables of development times, which give a ready guide to the periods required with all the principal makes of plates or films, for various temperatures and with specified strengths of developing-baths.

(v) *Fixation*. The plate is then placed in a solution of sodium thiosulphate ('hypo') containing 80 grams, hypo dissolved in 400 ml. water and kept there for 10 minutes.

(vi) *Washing* is the next stage, and is best carried out by placing the plate for half an hour in a vessel through which water is flowing, entering at the top and being drawn off at the bottom (e.g. by a siphon). Frequent change of water for an hour is also effective. After washing the negative it is placed on a drying rack in a position free from dust and allowed to dry. This completes the preparation of the negative.

(vii) *Printing*, or the formation of a positive from the negative, is accomplished by placing the negative in contact with printing paper or a lantern slide in a printing frame—making sure that the gelatine surface of the plate is in contact with the sensitive side of the paper or slide—and exposing to light. The underlying slide or paper is more or less protected from the light where the negative is densest, and most exposed where the negative is thinnest. A reversed image of the negative or a 'positive' results, corresponding to the distribution of light and shade in the original subject. The correct exposure (artificial light is generally used) is best determined in a similar manner to that already described in copying. For this a piece of card can be held in front of the frame and strips of the surface successively covered. Lantern slides are developed, fixed and washed in the same way as plates. For the development of lantern slides a hydroquinone developer may also be used. This should consist of water 1 litre, sodium sulphite 20 grams, sodium carbonate 60 grams, hydroquinone 10 grams and 10 ml. of a 10 per cent solution of potassium bromide. With a slide of average exposure the development should take from 5 to 6 minutes at 20°. For papers much the same holds, but different developers and different times of development, &c., may be necessary for the best results. Instructions will be given by the makers in each packet.

**Intensification and Reduction.** If a faulty negative is obtained through incorrect exposure or development it is always best to repeat the exposure. Sometimes, however, this is impossible, and it is necessary to make the best of the existing negative. Improvement in this can often be accomplished by processes known as reduction and intensification. Reduction is always carried out before intensification if it becomes necessary to apply both processes to the same negative.

*Reduction* consists of the partial removal of the silver image by formation of a soluble silver salt. Two reducers are in common use. The best known—Farmer's 'hypo-ferricyanide' reducer—contains hypo and potassium ferricyanide, and its action consists in forming silver ferrocyanide with the silver in the image, which dissolves in the hypo. The visible result is that the image gradually loses density. This reducer acts fairly evenly over the image irrespective of the densities and so reduces without altering contrast but if strong reduces the shadows at a greater rate than the high lights, but this does not actually increase contrast. The printing contrast is somewhat decreased even if the negative is made to appear brighter. The second reducer, ammonium persulphate, is decidedly selective; it attacks the high lights at a greater rate than the shadows, and enables density and contrast to be reduced together.

*Farmer's solution* consists of a 20 per cent solution of 'hypo' to which sufficient 5 per cent potassium ferricyanide has been added to colour it lemon-yellow. The mixed reducer keeps very badly and loses its activity in a few minutes.

*Use.* The plate is thoroughly wetted with water, and placed for 1 minute in the freshly prepared solution, rocking gently. It is then lifted out, rinsed under the flowing tap and examined. If the density is correct further reduction is prevented by washing under the flowing tap for 20 minutes. If reduction is incomplete the plate is immersed in the reducer for another half-minute, passed under the tap, and re-examined.

*Ammonium Persulphate Reducer.* Sufficient 3 per cent ammonium persulphate to cover the plate is made up and placed in a dish. One drop of strong sulphuric acid is added by means of a glass rod and the whole stirred. The wet negative is then inserted. If no action takes place within 2 minutes, the negative is removed and another drop of sulphuric acid added as before. Reduction should now begin at once on reinserting the plate, and the change may be recognized by the appearance of a cloudy deposit in the solution. When this is seen distinctly the negative is removed, rinsed and examined, and if sufficiently reduced is placed for 2 minutes in a 5 per cent solution of sodium sulphite to prevent any further action and then washed.

*Intensification* consists in increasing the density and contrast of the negative by depositing more or less opaque material on the original silver image. The substances commonly deposited are mercury and chromium salts or complexes containing these. The mercury intensifier is the more active and gives marked increase of density and contrast; the chromium is less violent, and brings about a moderate increase in contrast such as may often adapt a negative to such a printing paper as would otherwise give rather too soft a print.

*The mercury intensifier* consists of two solutions: (i) Mercuric chloride (strength immaterial); (ii) 8 per cent aqueous ammonia.

The well-wetted negative is placed in the first solution and left until the image is completely bleached both on the face and back, then washed under the tap for at least 10 minutes and placed in the ammonia solution. The image darkens. When the back of the negative is blackened completely the plate is removed and washed in water for 5 minutes. The mercury solution may be poured back into the bottle and preserved for future use. The

mercury ammonia intensifier does not give a permanent image. To obtain a permanent image the plate should be developed, after bleaching, in any non-staining alkaline developer. The intensification is, however, less than that for ammonia.

*The chromium intensifier* consists of two solutions :

(i) A saturated solution of potassium bichromate to which is added one-fiftieth of its volume of 10 per cent hydrochloric acid solution.

(ii) Sodium sulphite crystals (100 grams) dissolved in 300 ml. water to which is added 7 grams amidol powder to make up to 300 ml.

The plate is bleached in the bichromate solution and washed with water until all traces of yellow coloration are removed. It is then placed in solution (ii) and should be exposed to daylight or strong artificial light or it may not darken properly. When blackened completely back and front it is removed, washed for 10 minutes and dried.

*Use of Reduction and Intensification.* Reduction with persulphate is the best remedy for over-development, and with Farmer's solution for over-exposure (if development has been normal). If an over-exposed plate has been under-developed it may need intensification to impart contrast. Intensification is also the proper remedy for want of contrast caused by under-development in a correctly exposed plate. To under-exposed plates little can be done.

**Photomicrography.** The outfit comprises camera, microscope, and illuminating system carried on a suitable backboard. Satisfactory work can be done with an ordinary stand camera, student microscope, condenser, and an incandescent light. The apparatus may be set up horizontally or vertically. The former is more convenient, but cannot be used in the photography of liquid preparations. It dispenses with the need for an optical bench. While the arrangements suggested may be of service to workers who have to improvise equipment inexpensively, the most complete and elaborate equipment is obtainable ready made from a number of makers of microscopic and other optical equipment.

*Microscope.* The main point is a firm stand, preferably of the claw or tripod shape, and coarse and fine adjustment free from back-lash. The inside of the tube should be 'dead' black to prevent reflections. A sub-stage condenser capable of up-and-down movement and an iris diaphragm are desirable. The best objectives to use are apochromatic, but the ordinary achromatic type works well, especially if monochromatic light or a yellow-green filter is used.

*Camera.* In general a half-plate long-extension bellows camera to take quarter-plates is most useful. The lens must be removed as the image is formed by the microscope. It is an advantage to be able to extend the camera from the back while the front remains fixed in position. A good ground-glass focusing screen is essential, and is best provided with one or two clear-glass spaces, when the image in the air may be viewed as in a plate-glass screen. A fine cross should be ruled on the front of the clear glass so that the aerial image will be located correctly. A simple and efficient form of light-tight connexion between camera and microscope consists of a black velvet sleeve with rubber bands for slipping on.

*Various Forms of Outfit.* (i) *Horizontal.* A solid base-board of seasoned

wood is required about 4 feet 6 inches long, 1 foot wide, 1 inch thick. The end of a second board should be secured by a screw to one end of this so as to be capable of rotating smoothly. This second board carries the horizontal microscope, illuminant, condensing system, &c., and allows these to be swung out clear of the camera for visual examination of the subject to be photographed, and for correctness of illumination, &c. Battens screwed to the rotating top serve as guides to keep the microscope and illuminant in line, and permit changes in their distance apart to be made. The end of the base-board remote from the rotating top carries the camera, which must be supported and clamped in such a position as to be in true alignment with the optical axis of the microscope, and to allow the bellows extension to work satisfactorily both forward (to facilitate attachment to the microscope) and backward (for accurate focusing on the screen). Success in photomicrography depends mainly on freedom from vibration or movement during the exposure. The table or bench carrying the apparatus should therefore be as steady as possible, and several layers of felt or similar material should be placed between it and the back-board.

(ii) *Vertical.* The simplest arrangement here is to support the camera (attached to a base-board) on a strong, rigid, four-legged stand (Fig. 38 (VIII)). The top pieces should be slotted so that the camera can fit exactly and firmly into them, and be easily removable. The base-board of the camera should fall firmly into place on the stand thus supporting the front rigidly and permitting any desired extension of the bellows. The microscope can be carried conveniently on blocks whose height will determine the camera extension and the magnification. Illumination presents no difficulty, as the microscope mirror can be oriented to make use of light coming from any convenient direction.

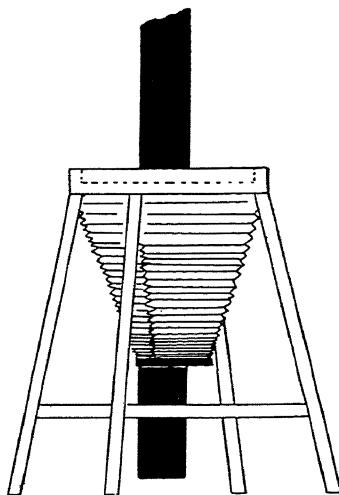


FIG. 38 (VIII)

*Illumination.* The electric arc, especially if automatic, is the best illuminant, but will require a water-cooling tank placed between the collecting lens and the microscope. Incandescent gas is frequently used, and is simple and convenient, though the tendency of the mesh of the mantle to show on the object to be photographed is a disadvantage. This disadvantage may be overcome by placing a sheet of ground-glass and an iris diaphragm in the path of the rays, but the intensity suffers greatly in that case. The mercury-vapour lamp is also satisfactory, and with appropriate screens forms a convenient source of monochromatic light. Ordinary electric filament lamps are not satisfactory, as the filament is so thin that a sufficiently broad image to fill the field cannot be obtained. The Pointolite lamp is an ideal illuminant for photography.

*Light Filters.* A green filter of narrow transmission in the yellow-green



region is valuable for improving the working qualities of achromatic objectives and bringing them nearer to those of apochromatics. Different-coloured filters are also used to increase contrast or to bring out detail in coloured objects. For increasing contrast a screen more or less complementary in colour to that of the object should be used, and for bringing out detail a screen of much the same colour as the object.

*Exposure.* The correct exposure depends on many factors: (1) the plate; (2) the illuminant; (3) the condensing system; (4) colour filters, if used; (5) the numerical aperture of the objective; (6) the magnification; (7) the extension of the camera; (8) the magnifying power of the ocular; (9) the colour, density, &c., of the object. The best plan is to obtain by a trial exposure of different strips (as explained earlier) the correct exposure for any one set of conditions. The slower types of fine-grained plate are best for microphotographic work. A card should be placed before the microscope objective and removed to make the exposure in order to avoid the disturbance of the system which might occur with other methods of exposure.

The photography of micro-crystals has to a large extent superseded schematic drawings. As pointed out by Oehlinger<sup>1</sup> while the drawing may be carefully executed, it is not sufficiently objective. For an excellent example of the use of photography, the work of Geilman<sup>2</sup> may be mentioned.

With the Contax camera<sup>3</sup> it is possible to watch a series of exposures which can show various stages of crystal formation even when these stages only remain for a very short period.

An excellent practical account of the use of photography in the laboratory, with its many applications, is described by Strong<sup>4</sup> in *Procedures in Experimental Physics* (Chapter XI).

<sup>1</sup> *Photographie und Forschung*, 1936, 5, 161.

<sup>2</sup> *Bilder zur mikrochemischen Analyse organischer Stoffe*.

<sup>3</sup> *Zeiss Ikon A.G., Dresden*.

<sup>4</sup> Prentice-Hall, N.Y., 1938.

## CHAPTER IX

### HIGH PRESSURE TECHNIQUE

#### SECTION 1: PLANT DESIGN

THE successful application of pressure by Haber and Le Rossignol to the synthesis of ammonia, by Patart to the production of methyl alcohol and by Bergius to the liquefaction of coal, has given great impetus to research on the effect of high pressures on chemical reactions, particularly in the field of organic chemistry. The need of apparatus capable of operating under the condition of high pressure combined with elevated temperature has given rise to a number of new considerations involving questions of design and choice of materials for the construction of apparatus required for such experimental work.

Most high-pressure apparatus is cylindrical in form; therefore a consideration of the elastic resistance of a simple cylinder is a necessary prelude to the study of high-pressure design. The principal stresses in an open cylinder due to an internal fluid pressure ( $P_0$ ) are a compression ( $P$ ) acting radially and a tensile stress ( $T$ ) acting tangentially. If the cylinder has closed ends a longitudinal stress is introduced but it is assumed that radial and tangential stresses are unaltered. The two latter stresses are both at a maximum at the internal bore as shown by Lamé's theorem <sup>2</sup> by which also the distribution of these forces throughout the cylinder wall may be calculated. If the internal and external radii and internal pressure are  $R_0$ ,  $R_1$ , and  $P_0$ , respectively, the following relationships hold for an intermediate radius  $R$ :

$$P = P_0 \{R_0^2 / (R_1^2 - R_0^2)\} \{(R_1/R)^2 - 1\}$$
$$T = P_0 \{R_0^2 / (R_1^2 - R_0^2)\} \{(R_1/R)^2 + 1\}$$

Values calculated for a cylinder having an external diameter twice its internal diameter are shown in Fig. 1 (IX).

Various suggestions have been made as to the best method of calculating the maximum pressure to which a cylinder may be subjected before it suffers permanent deformation. According to the 'principal stress' theory, where  $E$  = tensile elastic limit of the material,  $T$  or  $P$  is made equal to  $E$  according as  $T >$  or  $<$   $P$ . The 'maximum strain' theory predicts failure when

<sup>1</sup> This chapter was written by Mr. R. Taylor, M.A. (Cantab.), B.Sc. (Oxon), Senior Scientific Officer, Chemical Research Laboratory, D.S.I.R., Teddington. Part of the material is reproduced from an article by this author in 'J. Soc. Chem. Ind.', 1937, 56, 41T.

<sup>2</sup> *Leçons sur la Théorie . . . de l'Elasticité*, Paris, 1852. See Popplewell and Carington, *The Properties of Engineering Materials*, Methuen & Co., 1923, p. 217.

$T - \sigma P = E$  or  $P - \sigma T = E$  according as  $T >$  or  $< P$  (where  $\sigma =$  Poisson's ratio).

Guest<sup>1</sup> found, as the result of experiments on ductile materials under combined stresses, that the condition for yielding was the existence of a specific shearing stress, and that the intermediate principal stresses were without effect. Since  $T - P$  is the equivalent simple stress of a shear stress  $(T - P)/2$  resulting from the two principal stresses  $P$  and  $T$ , failure will occur<sup>2</sup> when  $T - P = E$ .

### PRESSURE AND TENSILE STRESSES IN A CYLINDER.

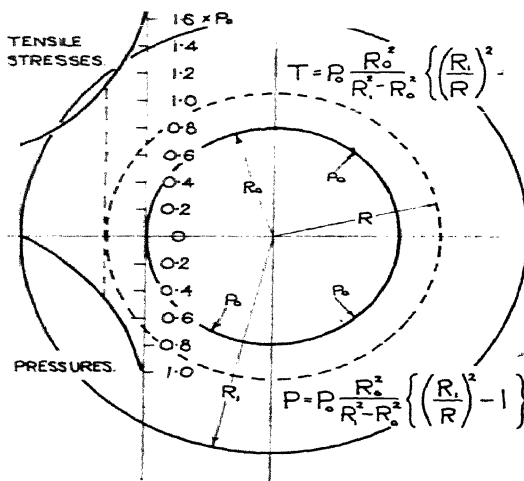


FIG. 1 (IX)

In the 'limiting strain' energy hypothesis presented by Haigh,<sup>3</sup> attention has been directed to the energy absorbed by the material in virtue of its elastic strain. This hypothesis has been employed by Imperial Chemical Industries in the design of their high-pressure vessels at Billingham.<sup>4</sup> The term 'limiting strain energy' signifies the quantity of energy that can be absorbed per unit volume of material uniformly strained to its elastic limit by the application of a specified combination of principal stresses. Calculations are made on the assumption that for any one material this quantity is independent of the nature of the simple or complex strain applied, and the results are in close agreement with the data obtained by Cook and Robertson.<sup>5</sup> The latter determined the pressures required to deform mild steel cylinders,

<sup>1</sup> *Phil. Mag.*, 1900, [v], 50, 78.

<sup>2</sup> See for fuller details A. E. Macrae, *Overstrain of Metals*, H.M. Stationery Office, 1930, Chapter I.

<sup>3</sup> *Rep. Brit. Assoc.*, 1919, 486.

<sup>4</sup> *Engineering*, 1911, 92, 786.

<sup>5</sup> Smith, *Engineering*, 1936, 141, 682.

and their experimental results were in agreement with the empirical formula  $P = 0.6E(k^2 - 1)/k^2$ , where  $k$  is the ratio of external to internal diameter. They regarded this formula as applying in general to ductile materials.

For brittle materials such as cast iron it is generally accepted that the maximum principal stress theory of failure should be applied

$$P = E(k^2 - 1)/(k^2 + 1)$$

In more recent experiments by Macrae<sup>1</sup> with various gun steels (nickel, chromium-nickel, chromium-nickel-molybdenum) the maximum radial elastic resistances of monobloc cylinders were found to be in close agreement with the 'shear' theory.

It can be shown by application of the shear hypothesis and Lamé's theorem that the limiting pressure  $P = E(k^2 - 1)/2k^2$ . It follows then that however thick the cylinder wall,  $P$  can never be greater than  $E/2$  and in practice little extra strength is obtained if  $k$  is made greater than about 4.

The limits thus imposed on the resistance of a cylinder to an internal pressure have been overcome by wire winding or by the shrinking on of one or more external cylinders. The conditions in a multiple built-up cylinder may be produced in a monobloc cylinder by the process of autofrettage. A radial pressure is applied on the bore and then released, and this pressure during its application sets up over-tension in some or all of the layers in the wall. In the words of Macrae,<sup>2</sup> 'the bore layer and some of the inner layers will be in states of residual compression, while the remaining outer layers will be in states of residual tension'.

Autofrettage treatment tests the homogeneous quality of the forging and predetermines its resistance to pressure more certainly than experiments on test pieces. The effect of shrinking on cylinders or of autofrettage is to reduce the resultant hoop stress at the bore so that the value of the radial stress  $P_0$  may more nearly approach that of the tensile elastic limit of the material, but however the vessel may be constructed, the internal pressure can never exceed the tensile elastic limit of the material without deformation occurring.

Temperature gradients in the cylinder wall may produce quite severe stresses, and Docherty<sup>3</sup> has evolved formulae for the principal stresses in a tube having a temperature gradient across the wall. For a steel tube  $k = 2$  and a temperature at the bore of 20° above that outside :

Hoop at bore	= - 2.56 tons per square inch (comp.)
" " outside	= + 1.64 " " " " (tens.)
Maximum radial stress	= - 0.35 ton per square inch.

The design of autoclaves or other high-pressure vessels necessitates a special study for each particular adaptation of the various conditions to be satisfied, but usually some type of steel is selected, since steel in general is the only material with the necessary high mechanical properties available at a sufficiently low cost. Steels employed in high-pressure plant include carbon steels, light alloy martensitic steels, and heavy alloy austenitic steels. The use of alloy steels, on account of their superior strength at ordinary

<sup>1</sup> Macrae, *op. cit.*, p. 120.

<sup>2</sup> *Op. cit.*, p. 33.

<sup>3</sup> *Proc. Inst. Mech. Eng.*, 1928, II, 923.

temperatures, permits the design of much lighter vessels which are also more resistant to corrosion than those of carbon steel.

At elevated temperatures there arises the phenomenon of creep, which Tapsell<sup>1</sup> defines as the deformation of a material occurring with time and due to an externally applied stress, whether the deformation be of the nature of plastic or of viscous flow. Steels required for service at high temperatures must consequently be tested at high temperatures.

Recent British research on the strength of metals at elevated temperature is described by Bailey, Dickenson, *et al.*,<sup>2</sup> who give the table (see on opposite page) for the effect of temperature on the stress required to give a certain rate of creep with a number of steels.

At lower temperatures the elastic limit is employed in calculations but at higher temperatures it is necessary to employ a limiting creep stress or some derived value. A large amount of most valuable data is being accumulated by the National Physical Laboratory which have been published in a number of Special Reports. These experiments are for the most part very protracted and one experiment may last several months. Methods have been adopted by the steel manufacturers to shorten the time required to obtain data, and to this end Hatfield<sup>3</sup> has devised an arbitrary set of conditions in order that short-period experiments may give a reliable index of the creep value of the material under test. He determines the particular stress which produces, at a certain temperature, an extension not exceeding 0.5 per cent of the gauge length during the first 24 hours and which within the next 48 hours is not sufficient to extend the test-piece further, at a greater rate than one-millionth of an inch per inch per hour. The results of this test he has called the 'time-yield' and Fig. 2 (IX) shows curves obtained by him for a number of steels with the following compositions:

	C	Mn	Si	Ni	Cr	Mo	W
Mild steel . . .	0.25	0.58	0.11	0.13			
Nickel steel . . .	0.24	0.55	0.20	3.3			
Nickel-chromium-molybdenum steel	0.30	0.57	0.24	2.38	0.61	0.59	—
Heat-resisting steel	0.50	0.60	0.50	9.4	12.68	—	3.75

This method has been adopted by the Brown-Firth Research Laboratories.

A different type of test, the Barr-Bardgett, employed in the laboratory of the United Steel Companies,<sup>4</sup> depends on the accurate measurement of the diminishing rate of creep in a stressed test-piece by means of a steel weigh-bar so arranged that the rate of decrease of the applied stress is proportional to the rate of creep of the specimen. It is claimed that results may be obtained in 48 hours which give safe stresses for the purpose of design, (i.e. stresses which will produce negligible initial deformation and permanence of dimension over long life).

In a Department of Scientific and Industrial Research Report<sup>5</sup> it is

<sup>1</sup> *Creep of Metals*, Oxford University Press, 1931, p. 31.

<sup>2</sup> *Symposium on Effect of Temperature on Metals*, Amer. Soc. Test. Mat. and Amer. Soc. Mech. Eng., 1931, 220.

<sup>3</sup> *Proc. Inst. Mech. Eng.*, 1932, 123, 773; *J. West Scotland Iron Steel Inst.*, 1928-9, 36, 60.

<sup>4</sup> *Purehete Creep Resisting Steel*, Samuel Fox & Co., Ltd., 1935.

<sup>5</sup> *Dept. Sci. Ind. Res.*, Eng. Res., Spec. Rep. No. 18.

Material	(Chemical composition, per cent.)							Stress to give a rate of creep of 0.00001 inch per inch per day, lb. per square inch.			
	Carbon	Nickel	Chromium	Molybdenum	Vanadium	Silicon	Tungsten	350° C. (660° F.)	450° C. (840° F.)	550° C. (1020° F.)	600° C. (1110° F.)
Mild steel . . . . .	0.20	—	—	—	—	—	—	22,500	14,500	4,500	—
Nickel-chromium steel . . . .	0.30	3.8	0.95	—	—	—	—	31,000	9,000	1,000	—
Nickel-chromium-molybdenum steel	0.28	3.5	0.87	0.24	—	—	—	56,000	33,500	2,000	—
Chromium-vanadium steel . . .	0.35	—	1.13	—	0.15	—	—	85,000	22,500	2,000	—
Chromium-silicon steel . . . .	0.61	—	8.32	—	—	2.62	—	53,500	25,500	4,500	—
Martensitic stainless . . . . .	0.27	—	14.00	—	—	—	—	49,000	27,000	4,500	—
Austenitic stainless . . . . .	0.16	8.0	18.00	—	—	—	0.6	—	14,500	6,500	4,500

pointed out that Staybrite (austenitic stainless) steel offers greater resistance to creep than other steels at similar temperatures, but owing to its low limit of proportionality, considerable permanent deformation occurs under high stresses. Thus, uneconomical working stresses must be adopted if such permanent deformation is to be avoided. The necessity is emphasized for consideration of creep characteristics at high stresses which produce fractures. Tests at high stresses permit the probable life of the steel under working

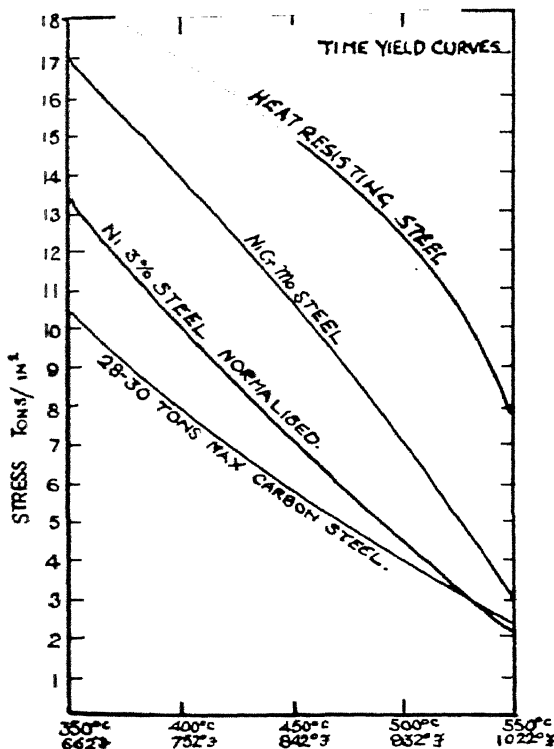


FIG. 2 (IX)

conditions to be estimated with greater certainty. It is further suggested in this Report that (with the exception of Staybrite) design stresses for temperatures of 300° and above should be deduced from the limiting creep stress curve in conjunction with a factor of safety of sufficient magnitude to bring the resulting stress at 300° to a value not greater than the limit of proportionality at that temperature.

The embrittlement of high-tensile alloy steels at elevated temperatures has been investigated by Goodrich,<sup>1</sup> who concluded that a mildly alloyed steel containing 0.6 per cent of chromium and 0.5 per cent of molybdenum yielded

<sup>1</sup> *Engineering*, 1936, 141, 651.

greatest resistance to embrittlement at  $450^{\circ}$  as shown by the notched-bar impact test. Increase in the nickel content appeared to decrease resistance to embrittlement of steels containing chromium and molybdenum and the higher was the total nickel and chromium content the greater was the molybdenum percentage apparently necessary to ensure relative freedom from embrittlement. Nickel-chromium-molybdenum steels of an average composition Ni 2.5 per cent, Cr 0.7 per cent, Mo 0.30 per cent are stated to have excellent properties up to  $500^{\circ}$ , but all the steels of this class creep very rapidly under stresses of the order of 200 atmospheres at  $550^{\circ}$ .<sup>1</sup>

Synthetic ammonia, methyl alcohol, and high-pressure hydrogenation all involve the use of hydrogen, and failure of mild steel under working conditions has led to the knowledge that when subjected to hydrogen at high temperatures it becomes decarbonized, extensive cracks are produced along the crystal boundaries, and there is finally severe disintegration. The resistance of various steels to hydrogen attack has been investigated by Inglis and Andrews<sup>2</sup> in a series of experiments lasting over 5 years. It was found that mild steel tube or forging in a coarse microstructural condition would have an indefinitely long life under 250 atm. at  $170^{\circ}$  or lower, and a nickel-chromium-molybdenum steel was definitely unsuitable for use in contact with hydrogen above  $320^{\circ}$ . Chromium steels were found to be most resistant to hydrogen attack. A 6 per cent chromium steel showed no hydrogen absorption or attack after 4,500 hours under 200 atm. at  $500^{\circ}$  and its physical properties were unimpaired. Chromium-nickel austenitic steel with hydrogen under 250 atm. pressure at  $450^{\circ}$  after 7,900 hours showed a high absorption of hydrogen (3.8 ml. per millilitre of metal), which caused considerable reduction in ductility and there was carbide precipitation at the grain boundaries.

Carbon monoxide attacks the surface of mild steels to give iron carbonyl. The rate of attack depends on the physical conditions of the surface but at ordinary temperatures, even under high pressure, the attack is usually slow. The presence of iron carbonyl in reaction gases is to be avoided since either it may act as a catalyst poison, or it may redeposit iron in the catalyst and thus bring about undesirable side reactions. Copper, silver, or aluminium linings are usually fitted to pressure plant employing carbon monoxide at temperatures above  $150^{\circ}$ . Steels of the 'Vibrac' type exhibit the same tendency as carbon steels but to a smaller degree. Highly alloyed steels such as Hadfield's C.R.I. appear very resistant to carbon monoxide attack even at temperatures approaching  $500^{\circ}$ .

In the design of structures subject to high stresses the factor of safety employed must allow for the possibility of lack of uniformity and also for change of properties of the material with use.

<sup>1</sup> *Symposium on Effect of Temperature on Metals*, Amer. Soc. Test. Mat. and Amer. Soc. Mech. Eng., 1931, 220.

<sup>2</sup> *J. Iron and Steel Inst.*, 1933, 128, No. 2, 383.



## SECTION 2: CONSTRUCTIONAL DETAILS

**Closures.** Various types of flanged connexions employing gaskets are shown in Fig. 3 (IX). Example A has a large interface and is suitable for low-pressure work. The higher are the pressures employed the greater is the necessity for the coupling stress to bear on a small interface. The joint faces in example B are raised and the surface of contact is thus partly reduced. The spigot and recess joint C is specially adapted for use with high internal

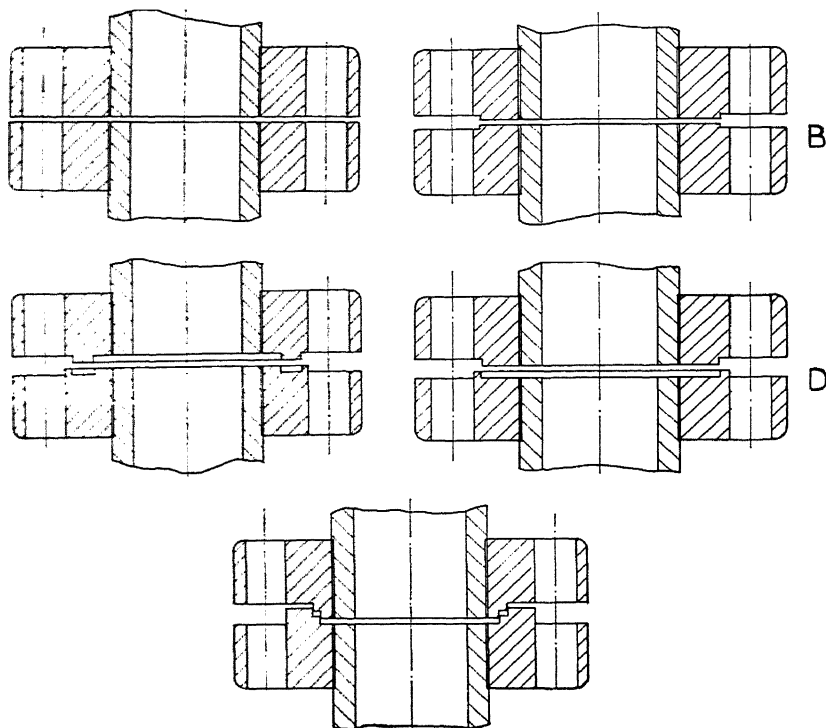


FIG. 3 (IX)

pressure since a gasket is employed which is completely confined. Where conditions require removal of the gasket without damage to the joint face a modified form (D) can be employed. A single-sided spigot and recess type of joint (example E) is employed on the autoclaves built at the Chemical Research Laboratory. A soft copper gasket 0.03125 inch thick is fitted to a narrow joint face approximately 0.25 inch wide. As the copper gaskets work-harden they are preferably annealed before remaking the joint.

An annular knife-edge joint was used by Ipatiev <sup>1</sup> in 1904 in his apparatus (Fig. 4 (IX)) for studying catalytic reactions under conditions of high temperature and pressure. His limiting conditions were about 400 atm. pressure and 625° temperature. A fresh copper gasket was used for each experiment. This type of joint is still employed, but a ball and cone arrangement (Fig. 5 (IX)) is to be preferred when the joint is frequently to be broken

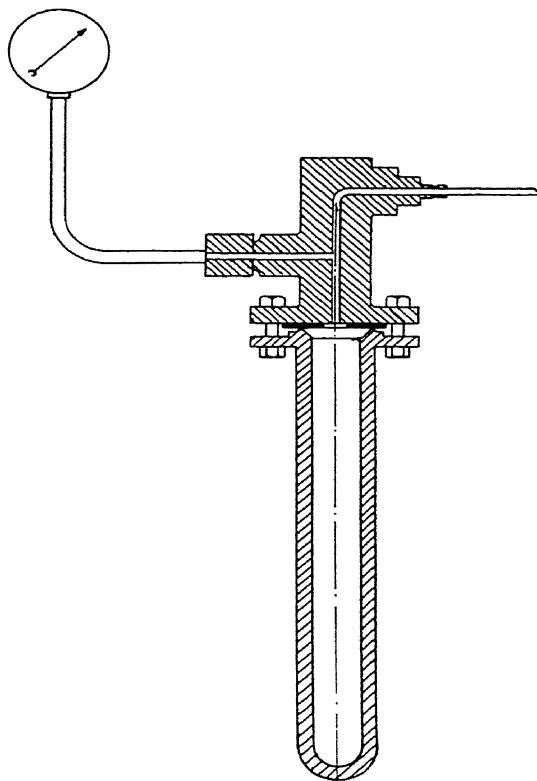


FIG. 4 (IX)

and remade. No gasket is here employed but line contact is obtained at which the strain is great compared with the force required to make the closure. The principle of line contact appears to have been first employed in the experiments of Haber and Le Rossignol <sup>2</sup> for their pioneer work on the synthesis of ammonia. The joint (Fig. 6 (IX)) comprises essentially two cones having inclusive angles of 16° and 20°, respectively, which are seated together with a line contact. A modern form of this type of joint as adopted

<sup>1</sup> *Ber.*, 1904, 37, 2961.

<sup>2</sup> *Z. Elektrochem.*, 1913, 19, 58; see also *ibid.*, 1908, 14, 181.

by H.M. Fuel Research Station <sup>1</sup> in their coal hydrogenation experiments is shown in Fig. 7a (IX). The plug has two conic surfaces which meet the wall surface each at an angle of  $7^\circ$  in a line contact. In such a joint deforma-

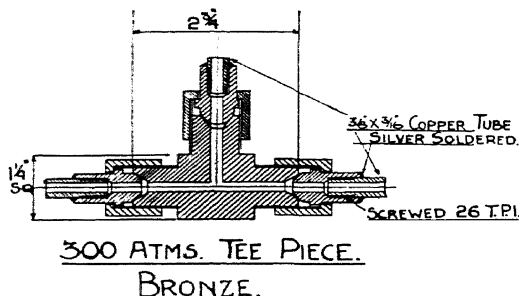


FIG. 5 (IX)

tion due to excessive tightening necessitates re-machining of the faces and allowance for this must be made in the design.

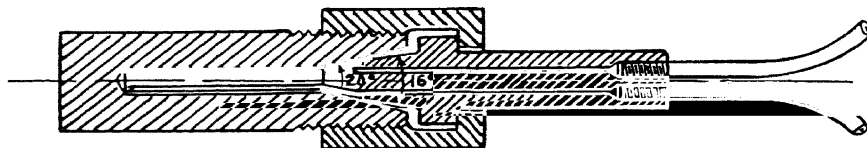
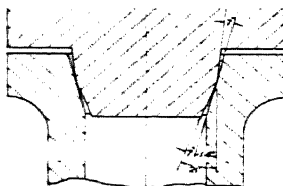


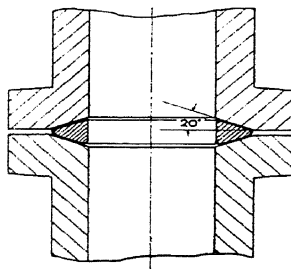
FIG. 6 (IX)

The lens ring method of closure (Fig. 7b (IX)) with line contact is often employed for high pressures since it is partly self-sealing. It may be



DOUBLE CONE PLUG JOINT

FIG. 7a (IX)



LENTIFORM RING JOINT.

FIG. 7b (IX)

regarded as an annular form of cone and ball joint. A method of applying the lens ring to large closures is disclosed in a patent of Synthetic Ammonia & Nitrates, Ltd.,<sup>2</sup> and an illustration reference is made in the patent to the

<sup>1</sup> Barber and Taylor, *Proc. Inst. Mech. Eng.*, 1934, 128, 5.

<sup>2</sup> B.P. 249,001.

covers of a cylindrical forging of internal diameter 4 feet, such as forms the shell of a catalytic apparatus for the synthetic production of ammonia, and the ring is generally made of mild steel.

The joints so far described (with the exception of the one involving the use of a lens ring) demand a definite initial stress in the closure mechanism at the joint face, and if the pressure exceeds this stress leakage will occur. For very high pressure the tightening mechanism may prove inadequate. The method of packing employed by Amagat (Fig. 8a (IX) ) in his classical

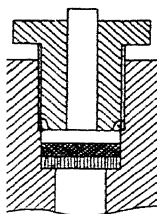


FIG. 8a (IX)

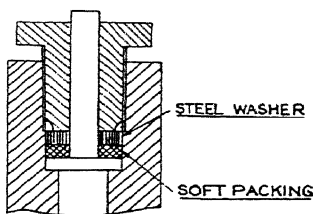


FIG. 8b (IX)

researches had this defect. All the packing described by Bridgman<sup>1</sup> in a paper on high-pressure technique is so designed that the effect of internal pressure is to make the packing still more tight (Fig. 8b (IX) ). The principle employed, which is capable of manifold modifications, is called the 'principle of the unsupported area' and in its application it will always be found that there is an area in the closure unexposed to a restraining force so that the hydrostatic pressure in the packing is always higher than in the compressed fluid. Bridgman has successfully employed such closures up to 20,000 atm. and beyond. The limiting factor to the pressures that may be employed appears to be the 'pinching-off' effect experienced by even solid cylinders under extreme pressure. Thus in the Bridgman type of closure shown, the force exerted on the central cylinder by the packing will bring about collapse, the cylinder will be 'pinched off', and the upper portion expelled. It is stated by Bridgman<sup>2</sup> that the maximum pressure a steel rod can withstand without 'pinching off' is numerically somewhere in the neighbourhood of the maximum tensile strength of the steel as measured by ordinary tensile tests.

The wave joint (Fig. 9 (IX) ), developed and patented by Manning and Imperial Chemical Industries,<sup>3</sup> is a very elegant and useful form of self-tightening joint which has been employed up to 3 inches diameter at extremely high pressures. It consists of two equal parallel sockets machined in the

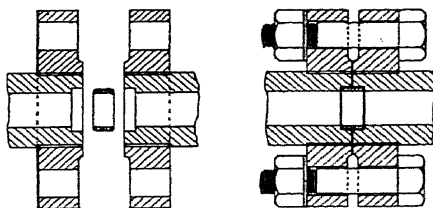


FIG. 9 (IX)

<sup>1</sup> *Proc. Amer. Acad. Arts Sci.*, 1913, 49, 627.

<sup>2</sup> *Physics of High Pressure*, Bell & Sons, Chapter II.

<sup>3</sup> *Engineering*, 1933, 136, 32; 1936, 141, 192.

parts to be joined, into which sockets a ring of wave section is forced to give an interference fit. The latter is necessary in order to give initial seating pressure until the self-tightening effect comes into play. The seating pressure in this joint is entirely in a radial direction and the axial force on the coupling never exceeds the thrust due to pressure on the socket area. This allows great saving in weight and cost. Mr. Manning has supplied the information that joints in good alloy steels working to 20 tons per square inch have been opened and closed a hundred times without either socket or rings being retouched in any way and without leak at the full or any intermediate pressure.

Mention must be made of the Vickers-Anderson joint ring which has been employed in the National Physical Laboratory's large compressed air tunnel, details of which have been kindly supplied by Mr. Relf, Superintendent, Aerodynamics Department.<sup>1</sup> The tunnel, designed to work under 25 atm., is composed of a number of rings each 17 feet diameter and approximately

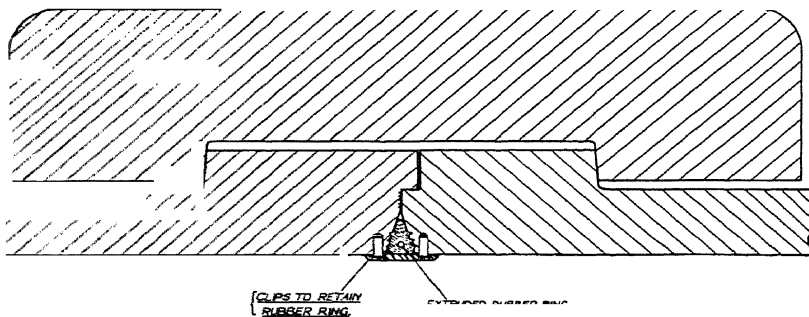


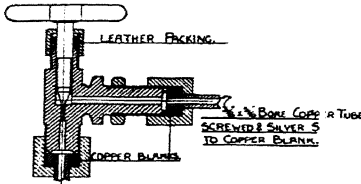
FIG. 10 (IX)

8 feet long; lips at the ends of these rings are tapered slightly and held together by circumferential butt straps each made in several pieces and joined together by longitudinal bolts. The ring ends (Fig. 10 (IX)) are so shaped as to give a V groove at their inner surface when joined together. The joint is effected by a hollow rubber ring pressed into the V groove and held in position by metal clips. The narrow end of the groove must have free access to the outer air, otherwise there is no unsupported area and the joint will leak. This type of joint has been used on a large converter 4 feet 9 inches diameter for coal hydrogenation at Billingham<sup>2</sup> and here the closure is made by a hollow steel ring held up to the V groove at the end of the section by a junk ring. Welded joints may be employed in construction of high-pressure plant if it can be established by inspection and other tests that the weld is sound; at Billingham pipe lines 3 inches internal diameter and 4.0625 inches external diameter, which have to be made of hydrogen-resistant steel with high alloy content, are made up from short lengths by electrical butt welding with subsequent normalization.

<sup>1</sup> See also *Engineering*, 1931, 132, 428.

<sup>2</sup> See for fuller details A. E. Macrae, *Overstrain of Metals*, H.M. Stationery Office, 1930, Chapter I.

**Valves.** The stop valve is an adjustable form of closure which is used for controlling the flow of gases. In Fig. 11 (IX) is shown a simple needle valve ;



300 ATMS. STOP VALVE.  
HYD TEST 3½ TONS SQ/INS.  
BRONZE BODY & CAP NUTS.  
MONEL METAL VALVE & SPINDLE.

FIG. 11 (IX)

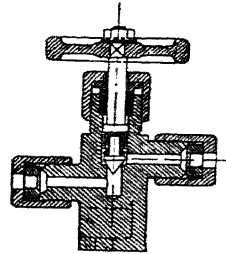


FIG. 12 (IX)

its body and cap nuts are of bronze, the valve and spindle are made of monel metal, and the packing around the spindle is leather. Fig. 12 (IX) shows a rather larger stop valve in which the valve itself is free to rotate in a brass bush screwed into the spindle ; any play between valve and spindle makes it difficult to open this valve in a regulated manner. A Hofer valve shown in Fig. 13 (IX) is designed to give very regulated control by means of a cone-faced valve which is continued in a parallel shank. The closure occurs at the lower end of the cone-shaped seating. The latter may be screwed out of the body for purposes of reconditioning.

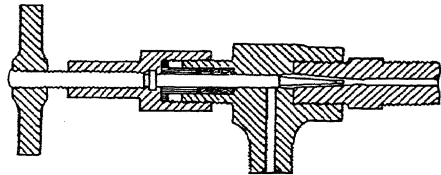


FIG. 13 (IX)

The principles employed in the construction of non-return valves as used

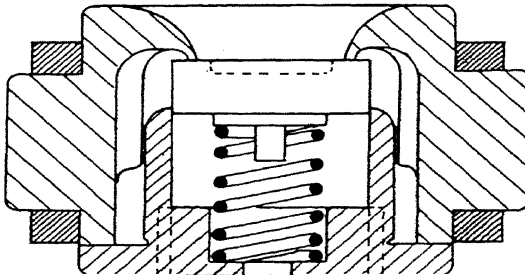


FIG. 14 (IX)

in compressor and circulator practice are shown in Figs. 14 (IX) and 15 (IX), which show the details of a valve from a Hofer compressor. The valve is a circular hardened steel disc and its ground surface is held up to the seat,

which is in the form of a very narrow annular ridge, by means of a light spring. In such a valve with adequate port area there is only a small lift and the hammer action is reduced to a minimum, thus ensuring long life. The valve is so constructed that it may be employed on either the suction or the pressure side of the cylinder.

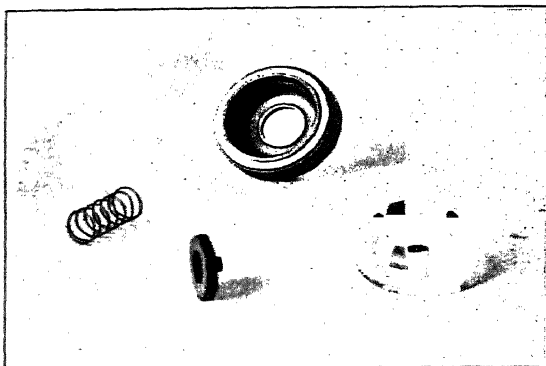


FIG. 15 (IX)

**Electrical Leads.** The introduction of electrical leads into a high-pressure vessel necessitates the construction of a closure with an insulating material. Since insulating materials in general do not possess a high degree of mechanical strength the maximum assistance must be given by the rest of the closure.

Barber and Taylor <sup>1</sup> have described the construction of insulated terminals for pressures of 200 atm. in which the coned shoulder on the lead bears on a fibre bush fitted into a coned seating in the terminal. It has been found necessary to prevent access of water to this terminal by means of a layer of heavy oil. Amagat had employed up to pressures of 300 kg. per square centimetre a similar type of electrode in which the insulating material was a coned shell of ivory. For the highest pressures Bridgman <sup>2</sup> has found it necessary to employ a much more complicated electrode with both rubber and mica insulation designed on the principle of the unsupported area.

The construction of a plug of high-chromium steel with Pyrex glass as the insulator has been described by Welberger.<sup>3</sup>

**Sight Glasses.** Amagat <sup>4</sup> employed a window made of a glass cone packed with ivory, similar in construction to his electrode, for pressures up to 1,500 kg. per square centimetre. Bridgman <sup>5</sup> has devised a window with glass in the form of a cylinder with rubber packers which withstood a pressure of 12,000 kg. per square centimetre, whilst Poulter <sup>6</sup> has designed a glass

<sup>1</sup> Barber and Taylor, *Proc. Inst. Mech. Eng.*, 1934, 128, 5.

<sup>2</sup> *Physics of High Pressure*, Bell & Sons, Chapter II.

<sup>3</sup> *J. Sci. Inst.*, 1933, 10, 247.

<sup>4</sup> *Compt. rend.*, 1887, 105, 165.

<sup>5</sup> *Physics of High Pressure*, Bell & Sons, Chapter II.

<sup>6</sup> *Phys. Rev.*, 1930, [ii], 35, 297.

window which employs no packing with which he has reached 30,000 kg. per square centimetre.

Barber and Taylor<sup>1</sup> have given the details of construction of a liquid indicator for working pressures of 200 atm. in which Pilkington's 'Armour-plate' glass was employed and celluloid was used as packing. A similar design has been adopted for the construction of a high-pressure housing for a fluid flow-meter to be mentioned later.

<sup>1</sup> Barber and Taylor, *Proc. Inst. Mech. Eng.*, 1934, 128, 5.



### SECTION 3: COMPRESSION AND CIRCULATION OF GASES

The arrangement of cylinders and glands of a four-stage compressor made by Andreas Hofer, Mulheim, Ruhr, is shown in Fig. 16 (IX). This compressor, which is designed for use with inflammable gases, is of convenient size for experimental purposes and will compress 5 cubic feet of gas per minute to 200–300 atm. pressure. The first stage, which is double-acting, and the second and third stages all have a piston sealed with cylinder rings. The last stage piston and the connecting-rod which passes into the second stage are both sealed by a gland packed with white-metal rings. All the stages are water-cooled and there are also inter-stage cooling coils. Lubricating oil from a drip feed is introduced into the first stage. Oil and water are separated from the compressed gas in the pressure vessel situated beyond the last stage.

The value of physical data for conditions of high pressure is clearly seen in

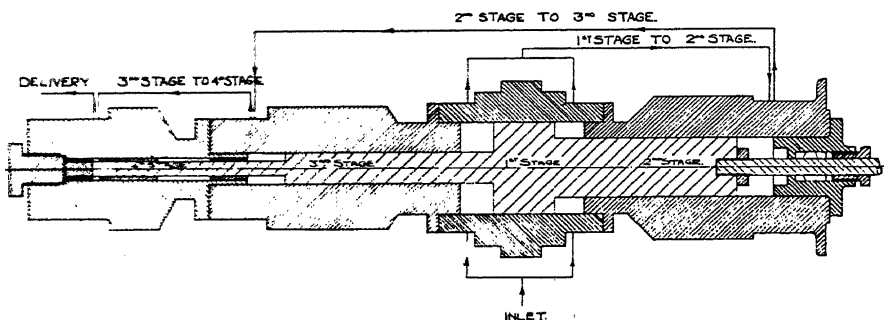


FIG. 16 (IX)

the design of compressors. Tropsch relates how Andreas Hofer came to him with a difficulty. The compressor he had made for use with hydrogen failed to work properly. Tropsch pointed out that he had not taken into account the compressibility of hydrogen and that the last stage should have been made 1.6 times larger. The suggestion was adopted by Hofer with immediate success.

The Hofer gas circulator is essentially a simple form of compressor and details of its construction are shown in Fig. 17 (IX).

Liquids may be introduced into plant under high pressure by means of a hand force pump such as is also used for hydraulic tests. A fuel injector pump, as employed on Diesel engines, has been found to perform the same operation mechanically and has proved successful even with methyl and ethyl alcohols.

Portable cylinders for the storage of gases are usually made of a mild

carbon steel but cylinders made of a light alloy steel such as Vibrac V 30 are more resistant to corrosion and can be constructed much more lightly. The two 3 cubic feet storage cylinders used at the Chemical Research Laboratory, Teddington, have an internal diameter 9.5 inches and wall thickness 0.5 inch and are made of Vibrac steel. Soft solid-drawn copper tubing 0.1875 inch

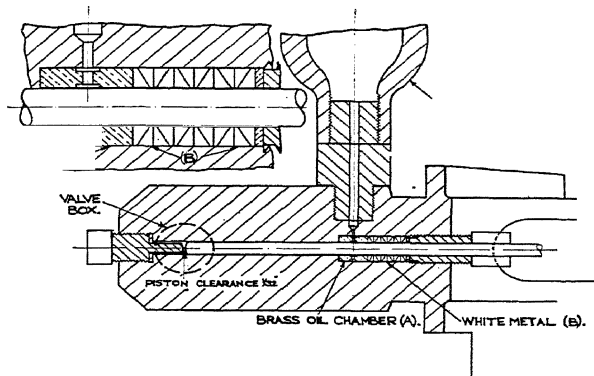


FIG. 17 (IX)

bore and 0.375 inch external diameter is used for delivering compressed gas as well as steel tubing with the same dimensions. Bridgman has stated that copper tubes 6 mm. external diameter and 1.5 mm. bore can be used up to 1,000 atm.

Preheater tubes have been made of Hadfield's C.R.I., outside diameter 0.725 inch and bore 0.1875 inch for use up to 500°

**Measurement of Pressure.** Pressure is conveniently measured by some form of Bourdon gauge, but since this is only a secondary standard it must be calibrated against a primary standard, usually a dead-weight pressure gauge. By means of the latter the force exerted by the pressure on a small piston is actually weighed. The essential details of such an instrument are given in Fig. 18 (IX). A is the piston of hardened steel; B is the cylinder turned out of a piece of tool steel and mounted on column C of mild steel, which is attached to the test apparatus. The spherical head of the piston carries an aluminium or brass tubular frame D with a ledge at the lower end to

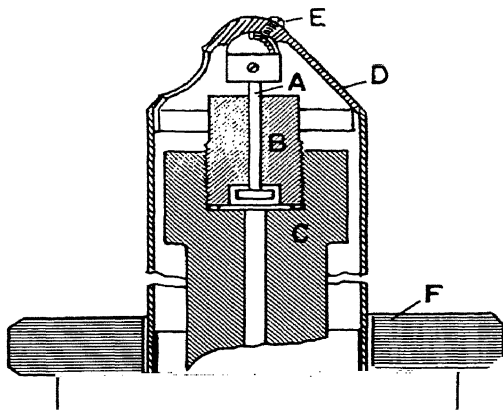


FIG. 18 (IX)

carry the annular weights of cast iron. The pistons vary in size from 0.2 square inch (for pressures up to 80 atm.) to 0.01 square inch for pressures up to 1,600 atm. Bridgman<sup>1</sup> has constructed gauges with pistons of smaller diameters for measurement of still higher pressures, and a differential form of dead-weight gauge has been designed by Michels.<sup>2</sup>

An orifice type of meter is generally employed for measuring the flow of gases and the differential pressure is usually determined by some form of manometer designed to work under high pressures. For this purpose various devices have been employed to measure heights in a mercury manometer. The height of the mercury may be determined by the making of an electrical contact; there may be several fixed contacts or one movable contact operated through a high-pressure gland. In the Bosch flow-meter<sup>3</sup> very fine tubing wound in coils transfers the pressure on either side of the orifice to a semicircular tube. The ends of the latter are connected by a yoke which is pivoted at its centre. Difference of pressure moves the mercury relatively to the semicircular tube and the whole suspension must rotate until the new centre of gravity is immediately below the point of suspension.

A flow-meter has been constructed at the Chemical Research Laboratory, Teddington, by supplying a glass rotameter tube with a high-pressure housing fitted with windows.

<sup>1</sup> *Proc. Amer. Acad. Arts Sci.*, 1909, *44*, 204.

<sup>2</sup> *Engineering*, 1933, *135*, 172.

<sup>3</sup> *Chem. Fabr.*, 1933, *6*, 127.

## SECTION 4: EXPERIMENTAL PLANTS

**Autoclaves.** The application of pressure to liquid phase reactions may speed up the process as the result of the higher temperatures then possible. Such reactions, besides many involving the use of gases, may conveniently be carried out in an autoclave. A rotating type of experimental autoclave is

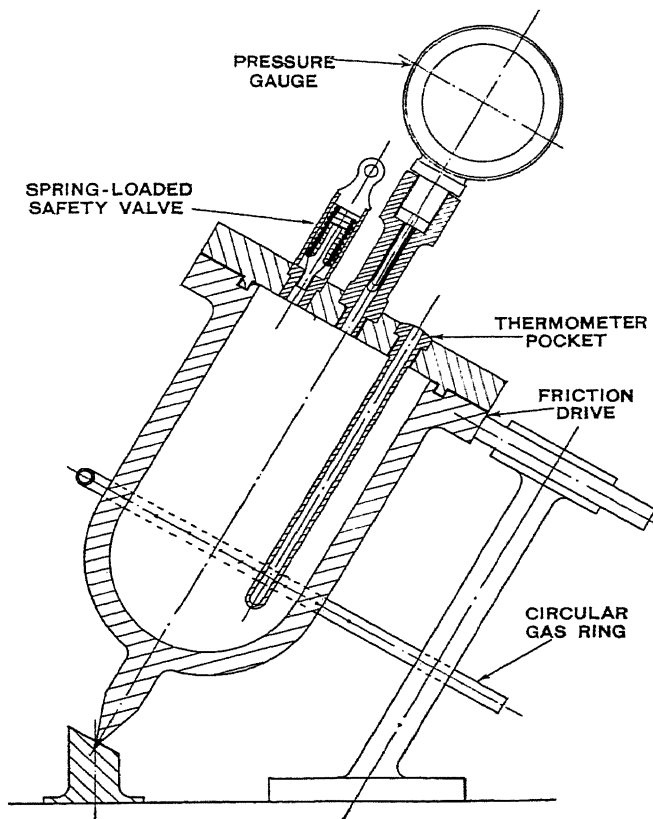


FIG. 19 (IX)

indicated diagrammatically in Fig. 19 (IX). The cover plate carries a pressure gauge, spring loaded safety valve and a thermometer pocket. This last assists in stirring the contents when the vessel is rotated by belt friction gear. Heating is effected by a gas-ring.

A second type of laboratory autoclave (Fig. 20 (IX)) is fitted with a stirrer. The latter passes through a gland provided with a brass oil chamber

or lantern ring (see Fig. 17 (IX) ), packed above and below with white metal and leather rings. Oil is fed into the lantern ring from a bottle which, as seen in the photograph, carries a pressure gauge and a pipe for equalizing the pressure above the oil with that in the autoclave. A water-jacket is provided to keep the gland cool. The liquid chemical reactants are usually placed in an open container which fits closely into the interior of the autoclave. For many purposes containers are made of 'staybrite' steel, but it may be necessary to employ a container made of silver, glass, silica, or enamelled iron. Two ports in the cover plate are fitted with valves for the passage and control of inlet and exit gases.

The joint between the autoclave body and the cover plate is of the type (Fig. 3 (IX) ) and the joint faces are V grooved to facilitate tightening on to an annealed copper gasket. Heating is external and is conveniently effected with gas. Here also the thermometer pocket assists in mixing the contents. An autoclave of this type made of 18/8 nickel-chrome steel may be operated up to 500° under a pressure of 250 atm.

**Flow through Plant for Liquid-gas Reactions.** Apparatus designed and constructed by Chemical Reactions, Limited, for the continuous hydrogenation of oil or tar is shown in Fig. 21 (IX), reproduced by kind permission of the Institution of Petroleum Technologists.<sup>1</sup> The liquid to be hydrogenated is held in a burette (1) and is forced by the pump (2) through line (3) into the top of the reaction vessel (4) under a pressure of 200 atm. The oil-system is freed from air prior to pumping the liquid by means of a high-pressure valve on line (3). Before entering the reaction vessel the oil is mixed with hydrogen entering through line (5). This hydrogen may come from a storage bottle or from a compressor. The reactants pass over the catalyst held in the vessel (4), then through the condenser (6) into the high-pressure separator (7). Hydrogen is released through valve (8) and the liquid product is drawn off from the bottom of the separator through valve (9) into a low-pressure expansion vessel where dissolved hydrocarbons can come out of solution.

The reaction vessel is simply a block of steel with a central boring and is heated electrically by an externally wound coil. A sliding resistance (10) controls the temperature.

**Converter for Gas Reactions.** The catalyst vessel depicted in Fig. 22 (IX) was designed for the study of catalytic syntheses from hydrogen and carbon monoxide. The pressure resisting shell is made of a nickel-chromium-molybdenum steel lined with a copper sheath to prevent the formation of iron carbonyl and the pyrometer pocket is similarly protected. The catalyst is held in a copper tube so fitted into the shell that the reaction gases must first pass up the annular space outside the copper tube before passing down through the catalyst. This counter-flow of the gases effects heat interchange which tends to maintain a low temperature gradient in the catalyst. All the joint faces are V-grooved and copper gaskets are employed.

The converter is electrically heated by an externally wound coil of nichrome tape. Such a vessel is incorporated in a circulatory type of apparatus which includes a gas circulator (see Fig. 17 (IX) ), preheater tubes, cooling coil and both high and low pressure receivers.

<sup>1</sup> Ormandy and Burns, *Petroleum*, 1933, II, 296.

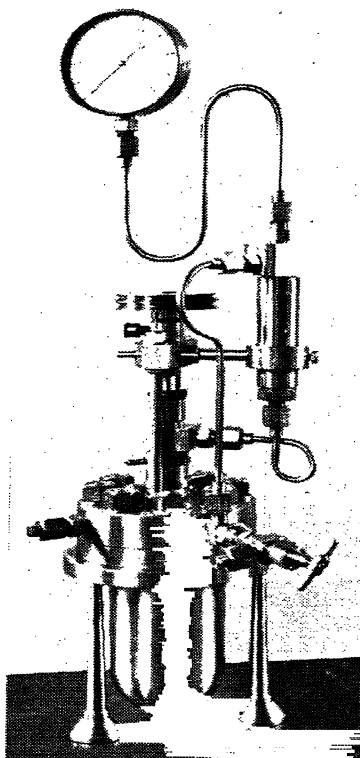


FIG. 20 (IX)

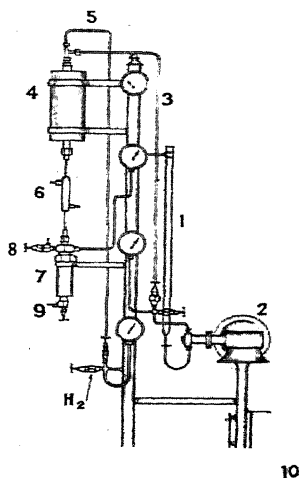


FIG. 21 (IX)

**Super Pressure Plant.** Messrs. Imperial Chemical Industries, Limited (Alkali), Northwich,<sup>1</sup> have constructed apparatus for the study of chemical reactions under pressures up to 12,000 atm. at temperatures not higher than 200° (Fig. 23 (IX)). It was made from Vibrac steel heat treated to give a tensile strength of 70 tons to 75 tons per square inch before machining. Autofrettage process was then applied in three stages with intervening heat treatment at 300° to 400°.

Substances to be treated are enclosed in small glass fittings sealed with mercury and placed in the reaction vessel (A). This vessel is joined by the connecting piece (B) to the cylinder (C) which forms the body of a hydraulic intensifier whose effective ratio is about 20 to 1. The high-pressure piston (D) is made of hardened steel ground to give a sliding fit and the packing is simply a rubber bung of slightly larger diameter than the bore. Connected to the upper end of the piston (D) is the low-pressure piston (E) which is provided with hydraulic cup leathers. An indicating stem (F)

<sup>1</sup> *Engineering*, 1933, 136, 32.

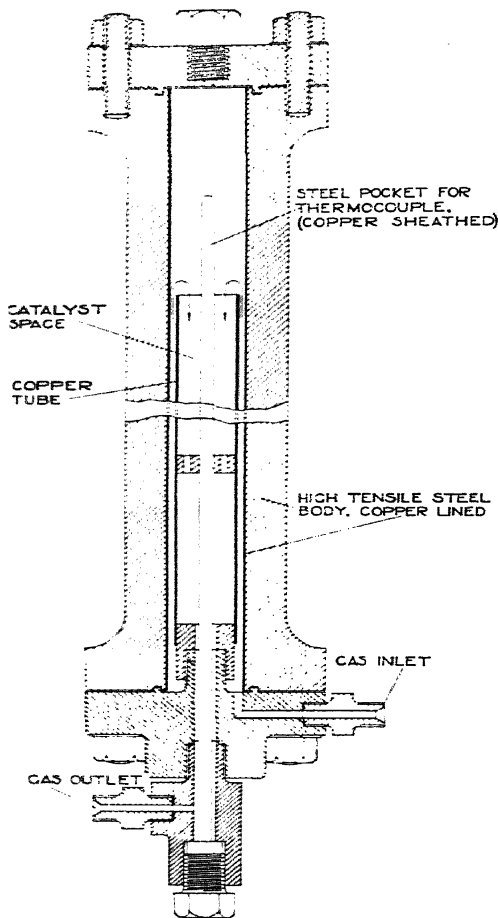


FIG. 22 (IX)

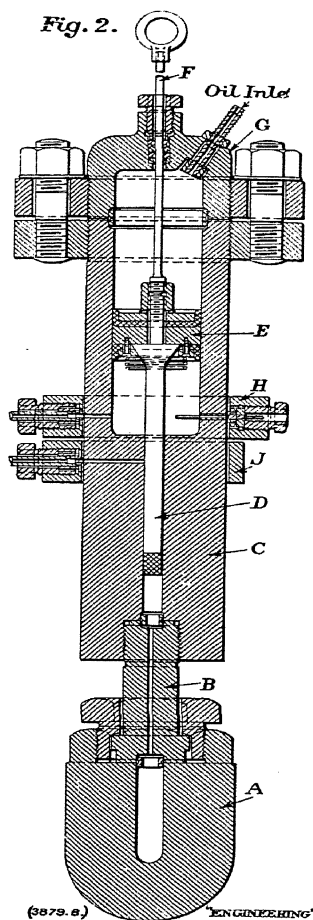


FIG. 23 (IX)

passed through a gland fitted with S.E.A. packing-rings. Two straps are provided to hold the radial connexions in order to avoid weakening the body by cutting screw threads. The upper strap (A) carries a pressure connexion for withdrawing the piston if it should stick, also an insulated rod which can make contact with a spring on the under side of piston (E), thereby completing an electrical circuit which rings a warning bell when the piston is near the bottom of its stroke. The joints on the small connexions are made with lens rings, and the manning wave ring is employed for the larger joints. The low-pressure side of the intensifier is supplied with oil from a small hydraulic hand pump. The space below the high-pressure piston is filled usually with

a light lubricating oil, but for the highest pressures at room or lower temperatures kerosene is used instead, since the lubricating oil would solidify.

### SAFETY PRECAUTIONS

Before pressure apparatus is put into use it is in general subjected to a hydraulic test in which deformation or other failure may be observed. The pressure of the test is in many cases 100 per cent over the working pressure. In the case of gauges 50 per cent excess pressure is considered adequate. Periodic measurement tests are also made to see if there has been any deformation with use, and a further hydraulic test is calculated to give warning of future failure. Pressure vessels may be protected by some form of relief valve, but in place of these, rupture discs are now frequently employed. Bonyun <sup>1</sup> has described the research carried out by Du Pont de Nemours & Co. in order to establish the rupture disc as the most adequate protection device for pressure vessels. Platinum is regarded as the best rupture disc material, inferior to none in the protection of unfired vessels, and data are given for the application of platinum, nickel, copper, silver, and aluminium. In the Hofer compressor, at the Chemical Research Laboratory, the oil and water separator bottle is protected by a rupture disc, and relief valves are fitted between all the stages.

In using high-pressure plant the limiting conditions of pressure and temperature must be known. Undue shocks and strains are avoided by making all pressure and temperature changes in a regulated manner, and temperature changes are preferably made under low pressures. Records made of the various variables throughout the use of the plant assist in the quick recognition of any unusual occurrence.

Circulatory plant for the testing of catalysts is conveniently situated behind steel plates on the front of which are fixed the various indicators and controls. Since the life of a gauge can never be guaranteed, observations are made indirectly by means of mirrors. A movable steel plate housing can be employed for autoclaves, and rope mantlets provided as an additional precaution.

The danger which arises from working with poisonous gas is met by a continuous supply of fresh air, which is maintained by a positive ventilation system supplemented by a suction fan which removes air from points most likely to be contaminated. For emergencies the equipment includes a short-distance breathing apparatus.

<sup>1</sup> *Chem. Met. Eng.*, 1935, 42, 260.





## CHAPTER X

### THERMOMETRY

#### SECTION 1: GAS THERMOMETERS

**UNIT of Temperature.** As the unit of temperature cannot be defined simply like the fundamental units of mass, length and time, and as there are several arbitrary units in vogue, the strict definition is postponed until after the following discussion.

**Fundamental Considerations.** Temperature may be defined as that state of bodies with reference to heat which controls the flow of heat among them when placed in thermal contact; of two bodies in thermal contact between which heat interchange is occurring, the one from which heat flows is said to have the higher temperature. All measurements of temperature depend on the fact that change in the quantity of heat which a body contains affects all its physical and chemical properties to a greater or less extent. In order quantitatively to compare the temperature of two bodies A and B, a third body C, the heat capacity of which is usually very small compared with that of A and B, is placed in thermal contact with, say, A. Heat adjustment occurs between A and C, the temperature of the former on account of its magnitude being taken to be practically unaltered in the process. When this adjustment is complete, as shown by a fixed physical property of C ceasing to alter, the final magnitude of this property is noted. C is then placed in thermal contact with B and the new value of the same physical property, when equilibrium is obtained, observed. The physical property chosen is one which is taken to alter regularly in the interval between the temperature of A and that of B; by comparing its two magnitudes we obtain the ratio of the temperatures of A and B.

The fixed body C with which the comparison is made is called a thermometer. In order to construct a thermometer a method of relating the magnitude of the measured physical property to the corresponding temperature is necessary. For this, two fixed points are taken at which a fixed substance undergoes a physical change of state; it is a property of substances which, apart from empirical observations, can be deduced from the phase rule that at definite temperatures, other external conditions being constant, their physical states alter with absorption or emission of heat. During this alteration of state or phase the temperature of the body does not alter, i.e. addition of heat produces no change in temperature but only a change in quantities of the two phases present. The two magnitudes of a physical property of a substance which between the two fixed temperatures do not change its physical state are determined for these two temperatures

and these values are then interpolated and extrapolated in a regular manner. These remarks as to temperature only apply to the body taken as a whole, which is all we are concerned with here. Fundamentally the temperature of a body is a measure of the mean kinetic energy, possessed in virtue of their motion, of the molecules or atoms of which it is composed—two bodies are in temperature equilibrium when the mean kinetic energies possessed by the particles of both are equal.

**Fixed Points.** The International Committee on Weights and Measures in 1887 took as the fixed points of a temperature scale the temperature at which pure ice melts and that at which pure water boils under standard pressure. Why water should be chosen as the fundamental substance is obvious. It is plentiful, is readily obtained pure, and its melting-point and boiling-point are easily determined, the necessary external conditions being readily obtained. For the interpolation and extrapolation of the interval between the points, initially the assumption has to be made that the substance employed suffers equal physical changes for an equal quantity of heat applied to it throughout the range to be graduated. However, the manifold agreements which result show the assumptions that certain physical properties of certain substances do alter regularly with temperature in the fundamental interval to be correct within narrow limits. Also there exists a standard scale entirely independent of the properties of any physical substance; it is called the absolute thermodynamic scale. (See below.) The deviation of certain scales from it can be deduced from theory (see later), and the limits determined to which the assumptions above are true.

**Thermometric Scales.** The International Committee on Weights and Measures in 1887 decided that the Centigrade scale of the constant-volume hydrogen thermometer should be standard, i.e. the interval between the melting-point and the boiling-point of water is divided into 100 equal parts called degrees, shown  $^{\circ}$ , by comparison with the pressures at constant volume corresponding to these temperatures of a constant mass of pure hydrogen gas, the hydrogen being taken at an initial manometric pressure, at the melting-point of ice, of 1 metre of mercury, that is 1.3158 times the standard barometric pressure. This scale is the normal gas scale; on it the melting-point of ice is taken at  $273.1^{\circ}$  and the boiling-point of water at standard pressure is  $373.1^{\circ}$ . It is much used experimentally in this ice-steam interval. Although this scale so obtained corresponds closely with the absolute scale, yet there are differences, and in 1913 the Fifth General Conference of Weights and Measures recommended the Absolute Centigrade Thermodynamic Scale should be substituted as the fundamental scale of temperature. This recommendation has been adopted by the National Physical Laboratory. Being absolute, its advantages are obvious and in precision work it should always be employed. For convenience the readings may be taken on other scales and reduced to this standard one.

**Absolute Scale.** It was Kelvin who first deduced the existence of the absolute scale by showing how temperature may be defined in terms of the availability of energy, and the definition made completely independent of the properties of any substance.

**Absolute Unit of Temperature.** This definition may be stated thus: If  $\theta_1$  and  $\theta_2$  are two absolute temperatures between which an ideal heat

engine is working in a perfectly reversible cycle, and if in the cycle it abstracts heat  $Q_1$  at the temperature  $\theta_1$  from an external source, does mechanical work  $Q_1 - Q_2$ , and delivers heat energy  $Q_2$  to an external source at a temperature  $\theta_2$ , then

$$\frac{\theta_1}{\theta_2} = \frac{Q_1}{Q_2}$$

**Absolute Centigrade Thermodynamic Scale.** And further, if  $\theta_1$  degrees be the temperature at which water has a vapour pressure of 760 mm. of standard mercury and  $\theta_2$  degrees be the temperature at which liquid and solid water are in equilibrium under that same pressure, then  $\theta_1^\circ - \theta_2^\circ = 100$ .

From this  $\theta_1^\circ$  and  $\theta_2^\circ$  can be deduced, and it is found that

$$\theta_1 = 373.1^\circ \text{ K}$$

and

$$\theta_2 = 273.1^\circ \text{ K}$$

Absolute degrees being represented as  $^\circ \text{ K}$ .

An ideal engine working as described between any temperature and the zero of the absolute scale will convert all the heat it takes in at the higher temperatures into work, and will give out no heat at the absolute zero.

From the above it can readily be shown that two bodies which are equal in temperature, as judged by the fact that an ideal heat engine working between them does no work, will not exchange heat if placed in contact.

A gas which obeyed the ideal gas law  $PV = R\theta$  absolutely would, if used in any of the three types of gas thermometers described below, give results identical with the above scale. Such an ideal gas can form the working substance of an ideal engine, the cycle being composed of adiabatic and isothermal expansions and contractions.

#### *Comparison of Thermometric Scales*

$$t^\circ \text{ C} = \frac{4}{5}t^\circ \text{ R} = \frac{9}{5}t + 32^\circ \text{ F.}$$

$$\text{C} = \text{Celsius (Centigrade)}$$

$$\text{F} = \text{Fahrenheit}$$

$$\text{R} = \text{Réaumur}$$

The gas constant (R) for 1 gram-molecule has the value (a)  $8.315 \times 10^7$ , (b) 1.988. For value in (a) energy is measured in ergs; in (b) it is measured in calories. Molecular volume = 22.32 litres.

**Gas Thermometers.** For accurate work it is the gas thermometer which is most often used to obtain the readings—the gas employed being one which shows small deviations from the gas laws. The results can be recalculated directly to the absolute scale from a knowledge of these small deviations, and in fact temperature measurement on all other scales must be compared with a gas thermometer to be reduced to absolute figures.

Theoretically the gas scale can be obtained by comparing either the change in volume of a constant mass of a gas at constant pressure, or the change in pressure of a constant mass of a gas at constant volume, or the change in mass of a gas kept at a constant pressure and volume, with the standard ice-steam interval, which is divided into 100 equal parts. The gas scale obtained in any of these three ways, if hydrogen or similar per-

manent gas be employed, agrees closely with the absolute scale in this interval: the maximum difference between the hydrogen constant-mass, constant-volume scale and the absolute scale is  $4.4 \times 10^{-2}^\circ$  at  $1,273.1^\circ \text{K}$ , where that between the nitrogen constant-mass, constant-volume scale and the absolute scale is  $6.46 \times 10^{-1}^\circ$ . The hydrogen constant-mass, constant-volume scale comes closest to the absolute, it being closer than the hydrogen constant-mass constant-pressure scale. The following table, due to Callendar, shows some of the differences: at ordinary temperatures they are small. The corrections for the constant-volume constant-mass thermometers vary somewhat with the initial pressure at  $273.1^\circ$ .

SCALE CORRECTIONS FOR CONSTANT-MASS GAS SCALES, ASSUMING  
TEMPERATURE OF MELTING ICE =  $273.1^\circ$

Temperature of triple point thermodynamic scale, $^\circ \text{K}$ .	Correction at constant press. = 760 mm.	Correction at constant volume, initial press. = 1,000 mm.		
	Hydrogen	Helium	Hydrogen	Nitrogen
123.1	- 0.084	- 0.026	+ 0.013	+ 0.195
173.1	- 0.022	- 0.012	+ 0.005	+ 0.080
223.1	- 0.006	- 0.004	+ 0.002	+ 0.024
273.1	- 0.002	- 0.001	+ 0.000	+ 0.007
293.1	- 0.0009	- 0.0008	- 0.0003	- 0.0043
313.1	- 0.0013	- 0.0011	- 0.0004	- 0.0059
323.1	- 0.0013	- 0.0011	- 0.0004	- 0.0059
333.1	- 0.0012	- 0.0011	- 0.0004	- 0.0054
353.1	- 0.0008	- 0.0007	- 0.0002	- 0.0038
423.1	+ 0.0029	- 0.0031	+ 0.0010	+ 0.0143
473.1	- 0.0068	- 0.0076	+ 0.0024	+ 0.035
573.1	- 0.0165	- 0.023	+ 0.0059	+ 0.088
723.1	- 0.034	- 0.047	+ 0.013	+ 0.189
1273.1	- 0.104	- 0.187	+ 0.044	+ 0.646

Besides being directly linked to the absolute scale and only deviating slightly from it, the gas thermometers possess other advantages; they have a great reproducibility, since the temperature coefficient of expansion of the material used in their construction is negligible compared with the coefficient of the gas, and so, apart from the gas itself, they are practically independent of the material employed, which is, however, usually reproducible. In this they are unlike, for example, the ordinary mercury thermometer, where there is the practical impossibility of reproducing the physical properties of a glass, and the coefficient of the latter is not negligible compared with that of mercury (see next Section). Again, owing to their relatively large temperature coefficients gas thermometers give sensible readings for very small changes in temperature. To illustrate, the coefficient of expansion of a gas with temperature is 100-400 times greater than that of most solids, 150 times

greater than that of glass, and 20 times greater than that of mercury. The range of temperature over which these thermometers can be employed is large—thus hydrogen and helium can be used at very low temperatures—the latter down almost to absolute zero; in the ice-steam interval the hydrogen constant-volume temperature is employed, as it shows the smallest deviations from the absolute scale. At high temperatures above  $800^{\circ}\text{K}$  hydrogen is unsuitable owing to its power of permeating substances under these conditions. No final agreement has as yet been reached as to which gas should replace it, but nitrogen, which does not pass through substances and for which the necessary corrections are small, has been employed in a vessel of pure iridium satisfactorily up almost to  $2,000^{\circ}\text{K}$ . However, helium would seem to possess advantages and has been suggested by Callendar; like nitrogen it does not pass through metals while its deviations from the absolute scale are less, and being a monatomic gas it cannot dissociate even at high temperatures. In fact its use would only seem to be limited by the material of which the thermometer is constructed. At these high temperatures the high pressure of the gas in the constant-volume thermometer may cause difficulties, but these may be lessened by working with a reduced initial pressure, e.g. 150–300 mm. of mercury at  $273.1^{\circ}\text{K}$ .

Air, though convenient in the ease with which it may be obtained, is unsuitable for use in standard gas thermometers owing to its want of constancy of composition and to the liability at high temperatures of the oxygen in it to attack the walls of the containing vessel or the mercury employed in the manometer portion of the apparatus.

**Constant-volume, Constant-mass Gas Thermometer.** One of the oldest accurate constant-volume, constant-mass gas thermometers was the apparatus used by Regnault to measure the coefficient of increase in pressure of a constant mass of gas at constant volume; for such an apparatus can conversely be used to measure temperature, if the increase in pressure be taken as a measure of the temperature. The gas, nitrogen, hydrogen, helium, &c., is contained in a globe or cylinder (Fig. 1 (X)) of suitable material, glass, porcelain, or metal, which is connected by a capillary via a three-way tap at D with a vessel B and open tube C, both containing mercury. By pouring mercury into C and adjusting tap at D (which is not shown in figure) to connect B to air, the mercury may be brought to D. A is then exhausted through D, being heated to an elevated temperature at least above the boiling-point of water to remove the last traces of gas and moisture. It is filled through D with the gas to be used, which is led in through a series of drying tubes. Exhaustion, heating and filling with dry gas are several times repeated, to remove the adsorbed moisture and gas from the inner surface of the globe. Finally, A being filled with dry gas at a desired pressure, it is brought, together with, say, the thermometer which is to be compared with the gas thermometer, into a zone the temperature of which is kept constant, say by

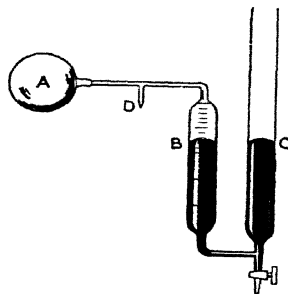


FIG. 1 (X)

melting ice. Tap at D is turned so as to connect B with A, and mercury run through D or poured in at C until its surface in B just touches an index consisting of a piece of black glass not shown in the figure. The difference in level between the mercury in B and C is measured by means of a cathetometer and the barometric height observed, as the total pressure of the gas is the sum of these two quantities, each reduced to standard conditions. The temperature of the mercury, and apparatus apart from that of A, which is immersed in a thermostat, is read on a standardized thermometer. The latter temperature need not be known so accurately, as any variation in it has only a secondary effect. The gas may then be heated with the thermometer it is wished to standardize to the boiling-point of pure water under standard or known conditions of pressure, and the comparison again carried out.

Various other temperatures may similarly be determined by the pressure readings. Or the gas thermometer may be brought into the zones the temperatures of which it is required to estimate. The pressures are measured in the constant volume as described. Corrections are applied for the volume of gas in the capillary, and in B, which alters with the pressure applied. Allowance must also be made for the variations in the density of mercury with temperature, and for the cubical expansion of the globe due to the rise in temperature and increase of pressure of the gas; this is done by direct

measurement of the actual linear expansion by means of a comparator. All constant-volume gas thermometers are modifications of the above. They are usually arranged so that the reading of the barometer is unnecessary or at least that the barometric measurement plus the excess pressure on the gas is obtained as the height of a single column of mercury, thereby reducing the chances of error. We give two examples.

**Examples of Constant-volume, Constant-mass Thermometers.** The first, which is the instrument in use at the Bureau International des Poids et Mesures, is arranged as shown in Fig. 2 (X) for comparison of the ordinary liquid-in-glass thermometers with a gas thermometer in order to deduce the corrections necessary for the standardization of the former—an important operation. The bulb (which is not shown in the figure) contains the gas, hydrogen for ordinary temperatures, is made of platinum-iridium and has a capacity of about 1 litre. It is connected with the manometer by the

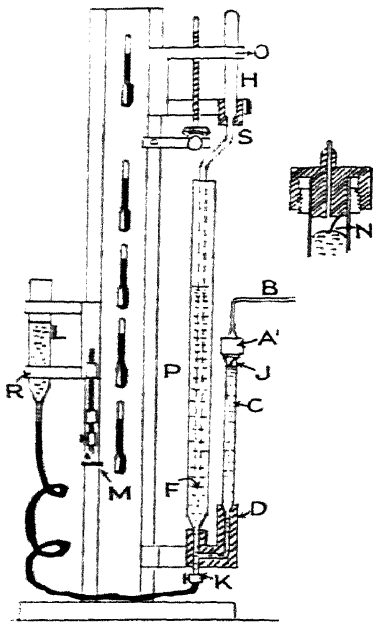


FIG. 2 (X)

capillary B, diameter 0.07 cm., length about 1 metre. For low-temperature

comparisons the thermometers to be compared are placed with the bulb in a large well-stirred water thermostat. For higher temperatures a constant-temperature vapour-bath is employed. B leads to a steel block A' hermetically sealed to a glass tube C which is also cemented into a steel block D, and sealed as shown to a second glass tube F also cemented in D. F has a three-way tap K at its lower end and is connected by a flexible steel tube with a movable reservoir L. The steel block D is fastened to a pillar P on which can move a cradle carrying a barometer tube H; the position of the cradle can be adjusted by the screw at S. The lower end of H dips into the mercury in F. The under-surface of A is flat except for the fine metal index—shown at N—which serves to mark a constant volume. The position of L is altered

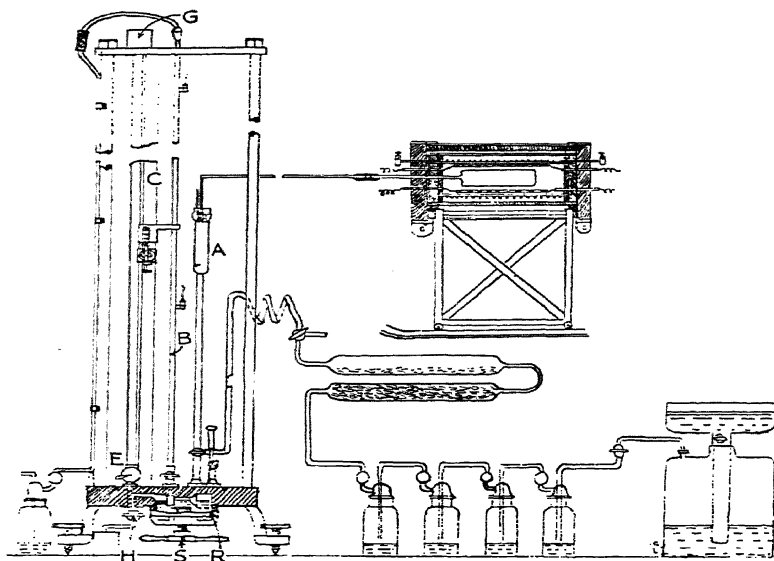


FIG. 3 (X)

by moving R by hand and then finally adjusting by means of M. The height of the column JH gives the total pressure on the gas and is measured by a cathetometer. To facilitate this it is arranged that H is vertically over J. The temperature of the column is determined by a number of standard thermometers. The method of working and the corrections to be applied are as described above. A similar thermometer was employed by Chappius in his classical researches on the gas thermometer, in which he compared the hydrogen, nitrogen, and carbon dioxide constant-mass, constant-volume thermometers with one another and with a number of standard mercury thermometers (see Section 2).

The second thermometer (Fig. 3 (X)) is the nitrogen gas thermometer of Holborn and Day. The bulb shown, which may be iridium, platinum, platinum-rhodium, or platinum-iridium, is connected by a flexible platinum



capillary tube with a vessel A which, together with a vessel B, is fixed into a closed mercury container R. By means of a steel tap H mercury can be withdrawn from R, while it can be added from the vessel G by means of the tube C and the steel tap E. Fine adjustments of the mercury column are accomplished by the screw S, which acts upon a thin steel plate forming the bottom of the vessel R. The apparatus can be adjusted to deal with high pressures for high-temperature work.

The mark, to which the top of the mercury in A is adjusted, consists of a short rounded needle in the plane underside of the nickel cap closing A. The needle is also of nickel so that it will not form an amalgam with mercury, and is only 0.4 mm. long, to make the gas space in A as small as possible. The cap in A is carefully fixed on by means of sealing-wax. The short glass projection shown in A serves if necessary for measurement of volume. B is 2 metres long and 12 mm. bore except at the wider portion, where it has a bore of 20 mm. It is fitted with a single-holed glass stopper and is connected with a wash bottle (lower left) which contains phosphorus pentoxide. To withdraw mercury when there is a reduced pressure in the gas space in A, the wash bottle is connected with a water pump and B evacuated. The scale for the pressure measurements is 1.87 metres long and is divided into millimetres: the vernier with which it is fitted reads to 0.2 mm. The error in the divisions is at most 0.4 mm. The manometer, as will be seen, is suitable for pressures moderately above and below atmospheric.

**Temperature Calculations on Constant-volume, Constant-mass Thermometers.** The calculation of a temperature from the readings on the constant-volume, constant-mass thermometer is simple. If  $P_i$  is the fully corrected pressure of a volume  $V$  of gas at the temperature of melting ice under standard conditions and  $P_s$  is the fully corrected pressure measured in the same units as  $P_i$  of the same mass of gas in the same volume  $V$  at the boiling-point of water under standard conditions, then from the definition of the thermometer it follows that:

where  $t_i$  is the temperature of melting ice and can at once be calculated; whence  $t_s = t_i + 100$  at once follows.

Again if  $P_t$  is the pressure at a temperature  $t$ , which is to be determined,

$$\frac{P_t}{P_i} = \frac{t}{t_i}$$

whence

$$t = \frac{t_i P_t}{P_i} = \frac{100 P_t}{P_s - P_i}$$

**Constant-pressure, Constant-mass Gas Thermometer.** A simple constant-pressure, constant-mass gas thermometer consists of a small glass bulb fitted with a capillary tube closed by a mercury index. The results obtained by volume observations from the motion of the mercury are not of great accuracy, as such an index does not completely enclose the gas, a film of gas persisting between the mercury and the walls of the tube. The

first accurate form of apparatus was devised by Regnault (see Fig. 1 (X), which is practically similar).

The globe A is connected by a capillary with the graduated tube B and the open tube C. The globe is filled with dry gas via the three-way tap at D as described above. The mercury is adjusted so that it is near the top of B. The bulb is then surrounded by melting ice or water at a fixed temperature and the level of the mercury in B and C noted. The pressure on the gas is the barometric height plus or minus the difference in the mercury levels in B and C. The globe is then heated to the temperature to be measured and mercury run out by the tap at the bottom of C until the difference in mercury levels in B and C is the same as before. The pressure on the gas is then the same as previously, the barometer being assumed constant. The position of the mercury in B is noted; the water bath round C and B is kept at a constant temperature determined by a standardized thermometer. The volumes of the globe and of the tube to the various positions of the mercury in B are obtained by filling with mercury or water and weighing. The corrections to be applied are of the same type as those described above.

**Temperature Calculations with Constant-pressure, Constant-mass Thermometer.** The calculation of a temperature from readings on the constant-pressure, constant-mass thermometer is similar to that for the constant-volume, constant-pressure thermometer:

$$t_i = \frac{100V_i}{V_s - V_i}$$

where  $t_i$  is the temperature of melting ice on the scale under investigation;  $V_i$  is the volume occupied by a given mass of gas at the temperature of ice melting under standard conditions, and  $V_s$  is the volume measured in the same units as  $V_i$  of the same mass of gas at the boiling-point of water under standard conditions.

Owing to the difficulties of measuring gas volumes at elevated temperatures the constant-mass, constant-pressure thermometer is not often employed. The constant-pressure, constant-volume thermometer (see below) is also difficult to realize practically, which is unfortunate, as the corrections which must be applied to reduce the reading on it to absolute figures are known more accurately with it than with the other two types of gas thermometers. However, these corrections are, as has been said, smallest with the hydrogen constant-volume, constant-mass thermometer, and as this is the most readily constructed and worked it is always employed. Beyond their use in standardizing technical thermometers gas thermometers are not used in industry; it is their academic and theoretical applications that are of importance.

**Callendar's Constant-pressure, Constant-mass Thermometer.** An apparatus suitable for use in the laboratory, in which some of the practical difficulties of the constant-pressure, constant-mass thermometer are overcome, has been described by Callendar. In this instrument (Fig. 4 (X)) the pressure of gas in a bulb A is maintained constantly, at the temperature under observation, equal to that of gas in another bulb C kept at a constant temperature in melting ice. The equality in pressure is observed by means of a sulphuric acid gauge D, the acid being placed in a U-tube with one arm

connected to each space. This eliminates all errors due to changes in the pressure and the like. The pressure on the bulb in the space is adjusted by

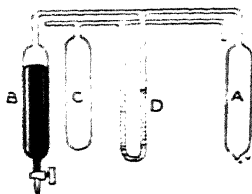


FIG. 4 (X)

running mercury out of a reservoir B connected to it. Errors arising from the uncertainty of the temperature of the connecting tubes are compensated for and eliminated by attaching to the bulb in melting ice a tube exactly similar in shape to that connecting the mercury reservoir to the thermometer bulb in the space the temperature of which is under observation. By weighing the volume of mercury withdrawn to adjust the pressure an accuracy of 0.1 of 1 per cent may readily be obtained at 400° K. In diagrammatic figure small tube from C should be shown similarly bent to tube leading to bulb B.

**Temperature Calculations with Constant-pressure, Constant-volume Thermometer.** Temperature readings with this thermometer are deduced as follows:

Let  $m_i$  be the mass of gas which exerts a given pressure  $p$  in a given volume  $v$  when at the temperature of ice melting under standard conditions,  $m_s$  be the mass of gas which exerts the same pressure  $p$  in the same volume  $v$  at the temperature  $t_s$  of water boiling under standard conditions, and let  $m_t$  be the mass of gas which exerts the same pressure and temperature at the temperature  $t$ ,  $m_i$ ,  $m_s$  and  $m_t$  being measured in the same units, and  $t_i$ ,  $t_s$  and  $t$  being temperatures on the scale under investigation.

Then, assuming the usual gas laws:

$$\frac{pv}{m_i t_i} = \frac{pv}{m_s t_s} = \frac{pv}{m_t t}$$

and

$$t_s - t_i = 100$$

whence

$$\frac{t_i}{t_s} = \frac{m_s}{m_i}$$

$$t_i = \frac{100m_s}{m_i - m_s}$$

and

$$\begin{aligned} t &= \frac{m_i t_i}{m_t} \\ &= \frac{100m_i m_s}{m_t(m_i - m_s)} \end{aligned}$$

Owing to its slight practical importance there is no necessity to describe actual forms of the constant-pressure, constant-volume thermometer.

**Fixed-point Scale.**<sup>1</sup> In order to facilitate the standardization of thermometers other than gas thermometers and to save the somewhat troublesome comparison with the latter, a fixed-point scale has been prepared in which the absolute temperatures on the international scale at which certain definite physical changes of state occur are set out. The following

<sup>1</sup> For general discussion on Thermometry see Ezer, Griffiths, *Methods of Measuring Temperature*; Griffin, 2nd ed., 1925, or later ed., and Thorpe, *Dict. App. Chem. Suppl.*, 1935, Vol. 2, p. 569.

table gives, up to  $1,100^{\circ}$  on the absolute scale, the fixed temperatures which are most accurately known. A few temperatures above  $1,100^{\circ}$  are also given, those marked with an asterisk being considered to be of the second order of accuracy. The temperatures are stated with the melting-point of ice under standard conditions  $0^{\circ}$  and the boiling-point of water under standard conditions  $100^{\circ}$ ;  $273.1^{\circ}$  must be added to each figure to obtain values on the absolute fixed-point scale. The accuracy and reproducibility of the various standard temperatures are also indicated, so that the present state of the science of accurate thermometry will be at once apparent.

	Estimated accuracy.	Reproducibility
B.P. of oxygen $-182.95^{\circ} + 0.01258 (p - 760) - 0.0000079 (p - 760)^2$ .	$0.50^{\circ}$	
Sublimation point of carbon dioxide $-78.5^{\circ} + 0.01595 (p - 760) - 0.0000111 (p - 760)^2$ .	$0.05^{\circ}$	
F.P. of mercury, $-38.87^{\circ}$ .	$0.05^{\circ}$	
M.P. of ice, $0^{\circ}$ .	by def.	$0.001^{\circ}$
Transition-point of sodium sulphate, $32.384^{\circ}$ .	$0.002^{\circ}$	$0.002^{\circ}$
B.P. of water, $100^{\circ}$ .	by def.	$0.001^{\circ}$
B.P. of naphthalene, $217.96^{\circ} + 0.058 (p - 760)$ .	$0.2^{\circ}$	$0.02^{\circ}$
B.P. of benzophenone, $305.9 + 0.063 (p - 760)$ .	$0.3^{\circ}$	$0.03^{\circ}$
*F.P. of tin, $231.84^{\circ}$ .	$0.2^{\circ}$	$0.03^{\circ}$
*F.P. of cadmium, $320.92^{\circ}$ .	$0.3^{\circ}$	$0.05^{\circ}$
*F.P. of zinc, $419.4^{\circ}$ .	$0.5^{\circ}$	$0.05^{\circ}$
B.P. of sulphur, $444.59^{\circ} + 0.0908 (p - 760) - 0.000047 (p - 760)^2$ .	$0.5^{\circ}$	$0.03^{\circ}$
F.P. of antimony, $629.8^{\circ}$ .	$1.5^{\circ}$	$0.3^{\circ}$
*F.P. of sodium chloride, $801^{\circ}$ .	$2.0^{\circ}$	$1.0^{\circ}$
F.P. of silver in a reducing atmosphere, $960.8^{\circ}$ .	$2.0^{\circ}$	$0.3^{\circ}$
F.P. of gold, $1062.4^{\circ}$ .	$3.0^{\circ}$	$0.5^{\circ}$
F.P. of copper in a reducing atmosphere, $1082.6^{\circ}$ .	$3.0^{\circ}$	$1.0^{\circ}$
F.P. of nickel, $1452.3^{\circ}$ .	$15^{\circ}$	$10^{\circ}$
F.P. of palladium, $1549.2^{\circ}$ .	$15^{\circ}$	$5^{\circ}$
F.P. of platinum, $1755^{\circ}$ .	$20^{\circ}$	$10^{\circ}$
F.P. of tungsten, $3000^{\circ}$ .	$100^{\circ}$	$25^{\circ}$

( $p$  = external pressure in millimetres of mercury under standard conditions. Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm. high having a mass of 13.5951 grams per  $\text{cm}^3$  subject to a gravitational acceleration of  $980.665 \text{ cm./sec.}^2$  and is equal to  $1,013,250 \text{ dynes/cm.}^2$ )

The scale of temperature is generally defined with reference to the apparent expansion of mercury in a glass container. For a standard practical scale of temperature preference is sometimes given to a scale defined with reference to one of the 'permanent' gases as thermometric substance. At the seventh International Congress on Weights and Measures held in Paris in 1927 the problem of adopting an exact thermodynamic scale for thermometry was realized. A scale known as the *International Temperature Scale* was adopted by the Congress for practical purposes. As far as is experimentally possible this scale approaches the true thermodynamic scale. Of course it is not final and with improvements in experimental technique or with the use of purer chemicals, different figures may be proposed from time to time. The suggested figures are fixed and can be obtained by the use of appropriate apparatus and substance. The following are secondary points:

B.P. of solid carbon dioxide	— 78.5°
F.P. of mercury	— 38.87°
F.P. of $\text{Na}_2\text{SO}_4$	32.38°
B.P. of naphthalene	217.96°
F.P.	231.85°
B.P. of benzophenone	305.9°
F.P. of cadmium	320.9°
F.P. of lead	327.3°
F.P. of zinc	419.45°
F.P. of antimony	630.5°
F.P. of copper	1,083°
F.P. of palladium	1,555°
F.P. of tungsten	3,400°

If temperatures are expressed on the scale of a well defined constant-volume hydrogen thermometer, 1° is regarded as the rise in temperature which will cause an increase of pressure equal to one-hundredth of the increase which occurs when the temperature rises from the lower fixed point to the higher.

Temperature-measuring instruments have been devised employing the above international temperature scale. Three instruments are employed to cover nearly the whole range. The platinum resistance thermometer is used for the range—183° to 660°, the platinum thermo-couple between 660° and 1,063° and the optical pyrometer for temperatures higher than 1,063°. The instruments are calibrated using the melting-point and boiling-point of a number of pure substances at fixed points as suggested at the International Congress. With the fixing of an International Standard Scale<sup>1</sup> of temperature it is no longer necessary to rely on gas thermometer observations for the establishment of a temperature scale. The International Scale conforms with the thermodynamic scale as close as is possible with present knowledge. The scale is based on fixed and reproducible equilibrium temperatures as explained above together with a definite technique for interpolation between the basic fixed temperatures.

**Other Methods of Measuring Temperatures.** Since the gas thermometer is not for practical purposes a convenient method of measuring temperature, other means are employed involving alterations in various physical properties. Where it is necessary for the purpose of accuracy, the readings by other methods can be related to those of a gas thermometer either by direct comparison or otherwise.

The practical methods of measuring temperatures are :

- (1) The apparent expansion or contraction with change of temperature of mercury in glass—other liquids are sometimes employed.
- (2) The change in the electrical resistance of certain metals—usually platinum, when heated or cooled.
- (3) The change in E.M.F. produced by heating or cooling one junction of two different metal wires, the other ends of which are electrically connected.
- (4) The measurement of the energy radiated from a heated body.
- (5) The change with temperature of the vapour pressure of certain liquids.
- (6) Other methods, e.g. change in E.M.F. of various cells with temperature, melting-points of substances, e.g. of cones of certain materials in pottery kilns, &c.

<sup>1</sup> Cf. *The Units and Standards of Measurement employed at the N.P.L., H.M. Stationery Office.*

## SECTION 2: MERCURY THERMOMETERS

The mercury thermometer is widely used for all measurements of temperature from  $250^{\circ}\text{K}$  to  $630^{\circ}\text{K}$ . Three scales are employed, but one—the Centigrade scale, introduced by Celsius—almost to the exclusion of the other two, being used altogether for scientific purposes and with one or two exceptions in industry. On the Centigrade scale the temperature of melting ice ( $273.1^{\circ}\text{K}$ ) is called  $0^{\circ}$ , and that of boiling water under standard conditions is called  $100^{\circ}$ ; the interval between is divided into 100 equal parts. The scale can be extended in both directions, each change in volume of the mercury one-hundredth of its expansion in the ice-steam interval being taken as equal to  $1^{\circ}$ . This cannot, however, be done if great accuracy be desired owing to the change of the coefficient of expansion of the mercury, calculated in absolute temperatures, with increase in temperature; direct comparison with a gas thermometer is then necessary to standardize the mercury thermometer. For temperatures below the melting-point of ice the scale is continued downwards from  $0^{\circ}$ , a minus sign (—) being prefixed to the readings obtained. When a temperature is recorded as  $X^{\circ}$  it is generally assumed that degrees centigrade are indicated.

The Fahrenheit scale, on which the melting-point of ice is  $32^{\circ}\text{F}$ ., and the boiling-point of water under standard conditions  $212^{\circ}\text{F}$ ., is still used in England for some commercial and meteorological purposes. The third scale, the Réaumur scale, is sometimes employed on the Continent; on it the melting-point of water is  $0^{\circ}\text{R}$ . and the boiling-point of water is  $80^{\circ}\text{R}$ . The methods of converting from one scale to the other will be obvious.

**Construction of a Mercury Thermometer.** The usual form of mercury thermometer consists of a glass bulb connected to a stem, which latter is traversed by a uniform capillary (see Fig. 5 (X) *a*). Such a thermometer is constructed by a suitable bulb having been blown and fitted with a suitable stem; the latter is constricted a little at the open end and a small funnel attached. Some pure dry mercury is placed in it and the bulb slightly heated to drive out some air and cooled to draw in mercury. The process is repeated until the bulb contains sufficient mercury. The latter is then boiled to drive out all air; on cooling with the open end immersed in mercury the bulb and stem become completely filled with the metal. The thermometer is then brought to a little above the highest point it is intended to measure and the top sealed in the blowpipe flame. In cooling the mercury contracts so that the stem is almost empty—the correct sizes of bulb and stem are known from experience. In order to prevent the mercury at high temperatures distilling to the top of the stem the space above the mercury is often filled with some inert gas, e.g. nitrogen, under pressure. The thermometer shown in Fig. 5 (X) *b* has a smaller reservoir of mercury with a

longer range for the same length of stem. It is less sensitive than thermometer shown in Fig. 5 (X) *a*.

To facilitate reading laboratory thermometers should be provided with a lens front as shown in Fig. 6 (X). It is also of advantage to back the glass with white enamel. This is impossible in a standard thermometer, which is read both from front and back to eliminate parallax errors.

**Graduation of a Mercury Thermometer.** The ice and steam points of a thermometer are then determined in the same way as described below for testing the fixed points of a given thermometer. The thermometer should not be graduated immediately on manufacture, for its bulb contracts in size rapidly for a few months and then more slowly; this slow contraction does not cease even after years. This is due to the gradual recovery of the glass from the treatment it receives in manufacture. Thus all the readings tend to rise and what is known as the 'secular change in the zero' is produced. The effect of the change can be minimized by keeping the thermometer before graduation at as high a temperature as it will stand for a few days, then at a slightly lower temperature, and so on until ordinary temperatures are reached—the glass recovering more rapidly at the higher temperature; in this way most of the error can be got over in a few weeks. The magnitude of this error varies with the glass used in the thermometer, e.g. in a thermometer of 'verre dur' it was  $-0.144^{\circ}$  to commence with, and  $-0.09^{\circ}$  after  $2\frac{1}{2}$  years, by which time the zero was only rising  $0.002^{\circ}$  per year as compared with an initial rate of  $0.04^{\circ}$  per year. In a thermometer made of crystal glass the rise was  $0.04^{\circ}$  the first 6 months; in  $2\frac{1}{2}$  years it had risen  $0.371^{\circ}$ ; and then it was rising at the rate of  $0.04^{\circ}$  in 6 months. Besides this error a temporary lowering of the zero occurs when the thermometer is

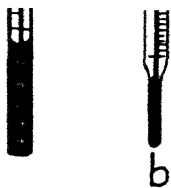


FIG. 5 (X)

brought to a high temperature owing to the bulb taking an appreciable time completely to contract on cooling. This will be discussed later.

The best glasses for thermometers—ones which will stand considerable wear, and show small changes in the zero—are Jena borosilicate glass 59 III and Normal glass 16 III. Thermometers made of the former are stamped 59 III; those from the latter have a fine red longitudinal mark on the back.

**Standardization of a Mercury Thermometer.** In a mercury thermometer what measures the temperatures is the difference between the cubical expansion of mercury and that of glass. If it were possible to make glass of absolutely constant physical

Direction for Viewing

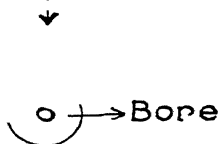


FIG. 6 (X)

properties and to construct from it thermometers of exactly similar dimensions, then a standard mercury thermometric scale could be defined. This is impossible, as scales defined in this way differ by as much as  $0.2^{\circ}$ ; so each thermometer as it is made is standardized and the errors in it are corrected with more or less accuracy according to the work for which it is intended. This re-standardization must be repeated each time the thermometer has to be employed for very accurate work.

**Essentials of a Standard Mercury Thermometer.** A good thermometer must be made of sound glass and must contain pure mercury. That is to say, by immersing the bulb in a quantity of sulphuric acid in a small vessel the temperature of which is gradually raised by means of a Bunsen burner the thermometer must not crack even when it is brought to a little above the highest temperature recorded on the scale. After heating, the inner glass wall of the capillary should remain perfectly clean; a bluish grey sediment or small bubbles adhering to it as the mercury falls back show that impure mercury was employed. Thermometers by good makers are usually satisfactory in these respects. The mercury thread must show no signs of breaking into sections at the higher points of the scale. Should it do so a nitrogen filling is required in the thermometer. This is not necessary in thermometers reading from  $0^{\circ}$  to  $100^{\circ}$ .

Being proved satisfactory in these essentials, an accurate thermometer must also satisfy the following conditions (Reichsanstalt: German Imperial Institute).

(1) The scale should be engraved on the outside of the stem, being scratched on it by a good file or a diamond in the laboratory only; more usually, and always in industry, the thermometer is coated with wax, and the divisions marked by exposing the glass corresponding to the scale divisions, and treating the thermometer with a solution of hydrofluoric acid. (Cf. Chap. II, S. 4.) In manufacture a large number of thermometers are treated together either with the liquid or being in a room and exposing to action of the gas. When etching is complete, the wax is removed and the etchings made to stand out by filling with graphite.

(2) The etched divisions must be equal in length.

(3) The maximum error in the length of a division must not exceed 5 per cent of that length and the lines marking the divisions must not be broader than 0.1 of the smallest division.

(4) The  $0^{\circ}$  and  $100^{\circ}$  points must be marked for testing purposes even though the thermometer be graduated only for use over a portion of the range.

In some German thermometers the stem is made very narrow and the scale is engraved on a separate piece of opal glass. This is attached to the stem at the bottom by a glass saddle and at the top by a spring which is fastened to it by a piece of fused glass. The spring allows for any expansion in heating. In other types of fastening the scale is hung from the top by a piece of glass. The whole is enclosed in a glass tube; in the second type of suspension care must be taken that the bottom of the scale is clear of the narrow portion of the glass case near the bulb. Should the scale be fastened by a tight-fitting cork sealed with gypsum the brass or nickel cap ought to be sealed with gypsum, and not with sealing-wax, otherwise the



thermometer may fall from the cap, if it is suspended from the latter while it is being heated. The graduation marks and numbers should be etched on this scale as described above. When a thermometer is held horizontally so that the scale reflects the light the finely etched divisions should be seen as depressed sharp straight strokes. The capillary must be fitted at the top with a pear-shaped enlargement in case of accidental heating above temperatures for which it is intended, and the whole must be void of air or other gas.

In addition to the above it is found that the length of a degree on the scale should be 6 to 7 mm. ; this degree should be divided into  $0.1^\circ$  intervals, which enables the position of the mercury to be estimated to 0.2 of a division by means of a telescope giving the temperature to  $0.02^\circ$ . To avoid a long stem two or more thermometers may be used to cover the range, e.g. one reading  $0^\circ$  to  $50^\circ$  and the other  $50^\circ$  to  $100^\circ$ . In both auxiliary reservoirs must be provided on the stem so that both the  $0^\circ$  and the  $100^\circ$  points can be marked.

**Corrections of Errors.** For each thermometer when made and graduated the following corrections have to be determined by experiment:

- (1) The scale correction to allow for errors in graduation.
- (2) The calibration correction to allow for inequalities in the bore.
- (3) The external-pressure correction to allow for alterations produced in the volume of the bulb by change in the external pressure.
- (4) The internal-pressure correction to allow for alterations produced in the volume of the bulb by changes in the internal pressure.
- (5) The zero correction to allow for the reading at the ice-point not exactly coinciding with the zero marked on the scale.
- (6) The fundamental correction to allow for the difference in the readings of the ice and steam points not being exactly  $100^\circ$  in the scale.

In addition the following have also to be determined:

- (7) The freezing-point depression after heating at  $100^\circ$  for half an hour and cooling in ice for 5 minutes.
- (8) The error in the reading due to only the bulb of the thermometer being at the temperature it is required to measure.

The maximum errors allowable are:

- (a)  $0.10^\circ$  in the fundamental interval;
- (b)  $0.25^\circ$  as the difference of the greatest deviations in the bore error;
- (c)  $0.10^\circ$  for the freezing-point depression after heating at  $100^\circ$  for half an hour and cooling in ice for 5 minutes.

The corrections for errors in the bore, fundamental interval, freezing-point and reduction to the standard scale are given separately to  $0.001^\circ$  and the sum of all corrections to  $0.01^\circ$ .

## DETERMINATION OF ERRORS

**Graduation Errors.** The errors in the graduation of the scale are best determined by mounting the thermometer on a good dividing engine which has itself been carefully examined for errors. Such an engine should also be used for the initial calibration.

**Error due to Inequalities in Bore.** The calibration of the thermometer tube is a matter of some difficulty. If the bore of a thermometer

were of exactly uniform cross-section throughout its whole length, equal lengths of the bore would everywhere have equal capacities so that if the stem between two fixed points were divided into  $N$  equal parts the volume of the bore between any two adjacent divisions would be  $1/N$  of the volume between the fixed points. Actually, however, the bore varies from point to point so that division of the capillary into equal lengths does not correspond to division into equal volumes. Since the volume change in the mercury is employed to measure change in temperature it becomes necessary either to place the divisions of the scale so that the distance between each division corresponds to an equal volume of the bore or else to divide the stem into divisions equal in length, and then to determine a series of corrections to be applied to the readings to allow for the inequalities of the



FIG. 7 (X)

bore. The latter method is usually employed. To carry out this calibration for the inequalities of the bore so that the scale is divided into sections of equal volume a thread of mercury 2 or 3 cm. long is drawn into the tube if the bore is to be tested before the thermometer is made—this is not recommended—or if the thermometer has been finished a short length of mercury is separated either by jerking as described below or by heating the column at the point where separation is required by means of a small gas jet 3 mm. high. This thread is moved to different parts of the tube and the length measured by means of a horizontal cathetometer (Fig. 7 (X)) ; since each of these lengths corresponds to the same volume of the bore equal to that of the thread of mercury, the tube can be divided into parts of equal volume. By using several threads in this way a tube can be calibrated very accurately. The exact details will be clear from what follows.

**Separation of a Mercury Thread.** To separate a thread of the required length the thermometer is held in the hand in an inverted position over the edge of the bench, and the wrist is brought down with a smart tap on the bench. This either causes a thread of mercury to separate from the rest or leaves a vacuum at the end of the bulb : in the latter case the thread is allowed to fill the stem and then the thermometer is turned up and again tapped. This should cause the bubble to move to the top of the bulb where it joins on to the stem. Before all the mercury has run back into the bulb the thermometer is inverted and another sharp tap given, and this generally succeeds in breaking off a thread. The latter



0 to  $(n-1)a$  scale divisions correspond to a temperature difference

$$(n-1)a \div (n-1)s - \bar{d}_1 \dots \bar{d}_{(n-1)}$$

0 to  $na$  scale divisions correspond to a temperature difference

$$na \div ns - \bar{d}_1 \dots \bar{d}_n$$

Hence  $ns - \bar{d}_1 \dots \bar{d}_n$  would be the correction to be applied at the last point if the zero were at  $0^\circ$ ; actually the zero is at  $p_0^\circ$ , and counting from this as zero the point  $na$  represents a temperature too low by  $p_0$ , so that the full correction will be

$$\text{at } na, p_0 \div ns - \bar{d}_1 \dots \bar{d}_n = D_n$$

$$\text{at } (n-1)a, p_0 \div (n-1)s - \bar{d}_1 \dots \bar{d}_{(n-1)} = D_{(n-1)}$$

$$\text{therefore by subtraction } D_n - D_{(n-1)} = s - \bar{d}_n$$

$$\text{and } D_n = D_{(n-1)} \div s - \bar{d}_n$$

**Accuracy of Calibration Method described Above.** This method of calculating the correction is not quite exact because  $\bar{d}_1, \bar{d}_2$ , &c., have been taken as temperatures while in reality they represent scale divisions. The corrections worked out apply not to the points  $a, 2a, 3a$ , &c., but more strictly to the points near these where the end of the thread actually rested.



FIG. 8 (X)

Further, some small parts of the scale will not be covered, while other parts will be covered twice. To illustrate the effect of this, if in the figure (Fig. 8 (X)) the thread be supposed to extend from 0 to  $D + p$ ,  $p$  being taken negative, and if between  $D$  and  $D + p$  a sharp irregularity (exaggerated in the figure) occur, it will not be corrected for in the expression deduced.

**Correction for Large Errors.** Unless the errors are large the method given above is sufficiently accurate for most purposes; if the errors are large the thread should be placed at 0 and the position at 'b' be determined, then the lower end should be put at 'b' and the other end will be at 'c', and so on all along; the corrections must now be worked out as before, but must be applied not at 0,  $a, 2a$ , &c., but at  $b, c, d$ , &c., intermediate points being found by graphic interpolation.

**The External-pressure Correction.** An increase of pressure above the normal barometric pressure is produced by an increase in the air pressure or by hydrostatic pressure on immersion in a liquid; the effect of this is to produce a small decrease in the volume of the bulb, forcing the mercury up in the tube, and giving too high a reading; a diminished pressure will produce the opposite effect. The external pressure coefficient  $\beta_e$  is the change in reading in scale degrees produced by a change in pressure of 1 mm. of mercury under standard conditions ( $0^\circ$  and  $45^\circ$  N. latitude). At the International Bureau the method of determining  $\beta_e$  is to place the thermometer in a glass tube containing sufficient mercury to cover the bulb; the remainder of the tube is filled with glycerine. The tube can be connected to an exhausted receiver or to the atmosphere. Arrangements are

made so that the temperature is gradually rising throughout the experiment, and readings are taken with the thermometer alternately exposed to atmospheric pressure and the reduced pressure, and from these observations the coefficient is calculated. It is usually between  $0.001^\circ$  and  $0.004^\circ$ .

**Internal-pressure Correction.** The internal-pressure error is due to the fact that the pressure at the centre of the bulb depends upon the height of mercury above it, which is much greater at high temperatures than low; so that at high temperatures the bulb is expanded and temperature indications will be too low. If the thermometer is always used in a horizontal position the error vanishes, provided the thermometer is not gas-filled, as is the case in  $0 - 100^\circ$  standard thermometers. The coefficient  $\beta_i$  is the change in reading in scale degrees for 1 mm. of standard mercury change of pressure; the value can be found experimentally for standard thermometers which are not filled with gas, by observations of the readings in steam in both the vertical and horizontal positions, and by the measurement of the distance between the centre of the bulb and the steam point. The two pressure coefficients are related as shown in the expression

$$\beta_i - \beta_e = 0.0000154$$

so that if one coefficient is determined experimentally, the other can be calculated. With a Beckmann thermometer (Chap. XIII, S. 2) the position of the mercury may alter as much as 0.5 cm. when moved from the vertical to the horizontal position.

**Determination of the Zero Correction and the Fundamental Interval.** The observations in steam are best made immediately before the ice point is determined. The apparatus used by Waidner and Dickinson consists of a double-walled steam jacket connected to a boiler containing pure water and some fragments of quartz to ensure regular boiling. The thermometer is suspended in the centre of the inner cylinder, the top of it projecting through a thin piece of rubber, so that a few tenths of a degree below the  $100^\circ$  point are visible. With this arrangement, in addition to the fact that the whole of the thermometer is not at the temperature of the steam, there is a tendency for mercury to distil into the vacuous space at the top of the tube: to avoid these difficulties an emergent stem heater was used, this consisting of a metal covering with plane glass windows through which the readings were taken. A steady stream of air was passed through a copper tube heated with a burner, and so into the heater; the temperature of the air in the heater could be read by means of a thermometer and was maintained at  $100^\circ$  by altering the rate of flow of the hot air. The whole apparatus could be tilted from the vertical to the horizontal, and readings taken in both positions. The temperature of the steam was obtained from the barometer reading corrected to  $0^\circ$ , latitude  $45^\circ$  N., sea-level and for capillarity, to which was added the excess pressure in the steam heater as obtained from a small manometer.

It is of course at a pressure of 760 mm. of mercury (measured at  $0^\circ$  at sea-level and  $45^\circ$  N. latitude) that the temperature of steam is  $100^\circ$ .

**Other Types of Apparatus.** A similar type of apparatus is shown in Fig. 9 (X). The steam rising from the boiling water in the lower vessel passes up the tube on the right into the inside tube which surrounds the

thermometer, then down and into the Liebig condenser where it is condensed and returned to the boiler through the tube on the left.

The ordinary thermometers in the laboratory, where the accuracy required does not necessitate the other corrections described, should have their steam and ice points determined at intervals, for with cheap thermometers the initial error may be  $0.5^\circ$  or more, and in addition there may be a large secular change in the zero. An apparatus (Fig. 10 (X)) suitable for general use consists of a two-walled vessel (A) made of copper; the thermometer to be tested is kept in position by a one-holed cork. The mercury should just be visible when the readings are made, while the bulb should be at least 20 cm. above the surface of the boiling water lest any of the latter spurt on it. To accomplish this with thermometers of various lengths the upper portion of the apparatus is made telescopic. An additional safeguard from the water is provided by placing a wire gauze across the vessel. As is well known, the temperature of boiling water is not a constant like that of steam, but depends to a certain extent on the nature of the vessel in which the water is contained and the presence or absence of dissolved substances.

**Zero Determination.** The zero of the thermometer is not a fixed point, but varies with the treatment of the thermometer; with an ordinary glass thermometer the zero may be depressed as much as  $0.2^\circ$  by heating to  $100^\circ$ . The lowering is approximately proportional to the square of the temperature to which the thermometer is raised; taking the figure cited,

$$-0.2 = k(100)^2$$

$$k = -0.2 \times 10^{-4}$$

so, that if

$$t = 10, dt = -0.002^\circ$$

and if

$$t = 50, dt = -0.05^\circ$$

For the special glasses used in making good-quality thermometers, the effect would be considerably less than this but is of sufficient importance to be considered when all the measurements taken with the thermometer do not fall within a few degrees.

The usual method is to determine the boiling-point first; then, after the thermometer has been maintained at  $100^\circ$  for 30 minutes, to take the

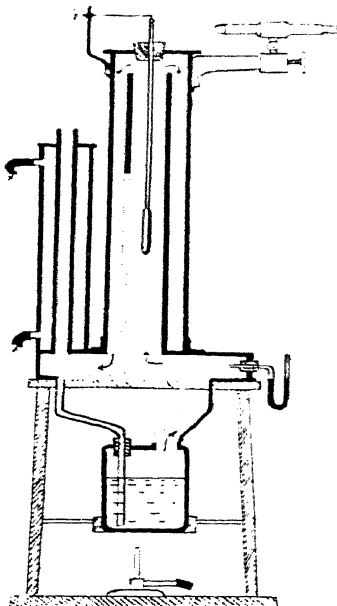


FIG. 9 (X)

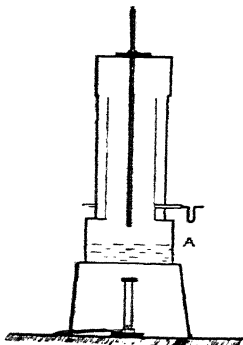


FIG. 10 (X)

zero. If, in subsequent measurements, the thermometer is raised to  $100^{\circ}$  before starting, the zero determined in the above way may be taken as the correct one. The procedure of Waidner and Dickinson in the determination of the zero was as follows: the thermometer was first heated in steam for the prescribed time; it was then removed from the steam and the time noted; the temperature was quickly reduced to about  $50^{\circ}$  by wiping with a damp cloth and the thermometer was then put in a super-cooler for about 15 seconds to lower the temperature to  $-2^{\circ}$  or  $-3^{\circ}$ , after which it was transferred to the ice bath. It was found possible in this way to commence readings within 90 seconds of the time of removal from the steam: for the next 3 or 4 minutes readings were taken alternately by two observers both with the scale in front of and behind the mercury. The supercooler was used with the object of allowing the mercury to reach the zero position with a rising thread, and consisted of a bottle covered with felt and containing a mixture of ice and salt in which was a test tube with sufficient mercury in it to cover the bulb of the thermometer.

**Ice-point Apparatus.** The ice-point apparatus was made of two glass vessels within a polished metal cylinder. Ice shavings made from carefully purified water were washed and placed inside both the vessels, that in the inner being kept well moistened with distilled water. Ice was heaped round the thermometer and a narrow channel was left to allow the readings to be taken; care was taken to set the thermometer in a vertical position and the telescope in a horizontal one and it was found advantageous to stir the ice by means of a small glass stirrer encircling the bulb of the thermometer. The purity of the ice was checked by measurements of the conductivity of the melted ice. The recovery of the zero commences at once after the removal from the steam; the value at the first instant cannot be determined, so that results are calculated to the value 3 minutes after removal from the steam. The only corrections that have to be applied are those for the internal and external pressures.

*Example.* As an example of the calculation of the fundamental interval the following may be taken:

Length of thermometer from $100^{\circ}$ to centre of bulb	= 527 mm.
Length of thermometer from $0^{\circ}$ to centre of bulb	= 60 mm.
External-pressure coefficient	= 0.0001080
Internal-pressure coefficient	= 0.0001234
External pressure	= 750 mm.
Zero reading	= $-0.090^{\circ}$
Steam reading, thermometer horizontal	= $99.638^{\circ}$
Steam reading, thermometer vertical	= $99.576^{\circ}$
Calculated steam temperature = $99.625^{\circ}$ , from pressure observations	
Calibration correction at $-0.090^{\circ}$	= 0.000
Calibration correction at $99.638^{\circ}$	= $-0.010^{\circ}$
Calibration correction at $99.576^{\circ}$	= $-0.010^{\circ}$
External-pressure correction = $10 \times 0.0001080$	= $+0.001^{\circ}$
Internal-pressure correction at $100^{\circ}$ in vertical position	
	= $527 \times 0.0001234 = +0.065^{\circ}$
Internal-pressure correction at $0^{\circ}$ in vertical position	
	= $60 \times 0.0001234 = 0.007^{\circ}$

*Calculation of Zero.*

Zero reading	=	- 0.090°
Calibration correction	=	0.000°
External-pressure correction	=	0.001°
Internal-pressure correction	=	0.007°
Therefore zero error	=	- 0.082°

		<i>Horizontal.</i>	<i>Vertical.</i>
Steam reading	=	99.638°	99.576°
Calibration correction	=	- 0.010°	- 0.010°
External pressure	=	0.001°	0.001°
Internal pressure	=	0.000°	0.065°
Zero correction	=	0.082°	0.082°
Corrected steam reading	=	99.711°	99.714°
Steam temperature	=	99.625°	99.625°
Error	=	0.086°	0.089°
Fundamental interval	=	100.086°	100.089°

The above shows the complete correction of a thermometer. These operations must be repeated at intervals owing to the secular change in the zero.

When the mercury thermometer is used for precision measurements at temperatures above 100° (this is not recommended) the ice point must always be redetermined, just as in the determinations of the steam point immediately after each reading at high temperatures, and the mercury corrections for the temporary lowering of zero above that obtained at 100° must be applied.

**Approximate Determination of Ice Point.** A simple apparatus for determining the ice point, where the very great accuracy indicated above is not required, is made by fitting to the stem of a large glass funnel a rubber tube closed by a pinch-cock, and filling the funnel with pure snow or pure finely powdered ice. A thermometer is then allowed to hang in the ice, which must reach to a little above the zero point—a space being left in front to determine the level of the mercury. Care must be taken to avoid pressure on the thermometer bulb of the mercury, as that would raise the zero point; for this reason too the thermometer must always be suspended in the ice and not stuck in it. The excess of water is run off from time to time, but the level in the funnel must be kept up. The constant position of the mercury is taken.

**Standardization by Comparing with a Standard Thermometer.** The process of complete correction of a thermometer as above is a very lengthy one, and it is more convenient to standardize a thermometer either by comparing the instrument carefully with a gas thermometer or with a mercury thermometer which has previously been carefully standardized.

The National Physical Laboratory undertakes the testing of precision thermometers, and this furnishes a very convenient method of obtaining a standard thermometer with which others in the laboratory may be compared. The method usually adopted consists of comparing the instrument under test with a series of standard thermometers immersed in well-stirred thermostats; from the known errors of the standards, those of the ther-



nometer under test can be determined, and these values, together with the ice and steam points, enable one to use a thermometer so tested as a sub-standard: if this is done it is of course necessary occasionally to check the fixed points. The N.P.L. will also test thermometers on the lines described at length above.

Thermometers with a N.P.L. certificate can be purchased and comparisons carried out in the laboratory. The standard and the thermometer under test are fastened together by two rubber rings cut from tubing of suitable width so that the middles of the two bulbs are on the same level. They are suspended in a large beaker containing water at the required temperature which is well stirred by a glass rod or with a mechanical stirrer or by blowing air through from the bellows of a blow-pipe. The thermometers are read at the same time. They must be adjusted so that the water is at the level of the top of the mercury column of the shorter; for the other a correction for the emergent thread (see below) is applied.

**Use of Mercury Thermometers.** In using mercury thermometers the conditions should be arranged so as to reproduce as nearly as possible those under which the corrections were determined, i.e. immersion up to the top of the mercury column, vertical position, reading with a rising meniscus, &c. When the temperature of a thermometer is falling, the mercury does not recede regularly but in a series of jerks: the meniscus can often be seen to remain still for a short time, and gradually alter the curvature of the surface; a sharp tap will then cause it to drop a considerable distance. The effect is much more noticeable with a falling column than with a rising one: whenever possible one reads with a rising meniscus and the tube is tapped before reading.

**Emergent Stem Correction.** When it is not possible to immerse the thermometer completely, it becomes necessary to apply a correction for the emergent part of the mercury column which is not at the same temperature as the bulb. Various equations have been proposed to correct for this error, but in practice none of them is satisfactory; the only practical method consists in making a series of tests with the thermometer under various conditions. Suppose a thermometer is required to read a temperature of  $t^\circ$ , a constant-temperature bath at this temperature is arranged and its temperature determined by a completely immersed thermometer; the thermometer under test is placed in the bath and readings taken with  $5^\circ$ ,  $10^\circ$ ,  $15^\circ$ , &c., of the stem outside the bath and a table of corrections is made. Such a table would only be of use when the external conditions, e.g. temperature, were the same as those during the calibration.

Where great accuracy is not required the equation—

$$T_c = T_o + 0.000156l (T_o - T_m), \text{ where}$$

$T_c$  = corrected temperature

$T_o$  = observed temperature

$l$  = length in degrees of mercury column, not at the temperature to be measured

$T_m$  = temperature of the middle point of the emergent thread taken by another short thermometer

can be used. As will be seen, the corrections depend on the length of the

mercury thread, not at the temperature to be measured, and on the temperature difference between the bulb and the emergent thread. The numerical constant is the apparent coefficient of expansion of mercury in glass.

If greater accuracy is required several thermometers at various parts of the thread are employed, and the mean reading taken to obtain  $T_m$ . For these readings short thermometers fastened to the main one with their bulbs in the desired position are convenient, or better still 'thread' thermometers of suitable length in which the capillary does not expand to a vessel at the bottom. Another arrangement is to surround the part of the thermometer not at the temperature to be measured, with a jacket through which a liquid or vapour of known temperature is circulated; the nearer the temperature of the jacket to the temperature which is being measured, the smaller the corrections.

Whenever possible, however, the whole thermometer to the top of the mercury column should be put in the enclosure the temperature of which it is required to measure, for the correction is often considerable, as will be seen from the following approximate rules.

**Approximate Rules.** For a difference of  $100^\circ$  between the temperature of the bulb and that of the middle of the thread the correction is  $0.1^\circ$  for each degree of emergent thread.

For  $200^\circ$  difference  $0.2^\circ$  is allowed for every 1 degree emerging. Any widening in the thread of mercury so as to show the  $0^\circ$  and  $100^\circ$  points (see earlier) in a thermometer of a limited range must always be completely immersed, as they are, so to speak, a part of the bulb. Complete tables of the corrections for thread immersion with thermometers of Jena or resistance glass will be found in Landolt-Börnstein's *Physikalisch-Chemische Tabellen*. Temperature readings which have been thus corrected are often followed by the abbreviated term: (Corr.).

**'Verre Dur' Mercury Scale.** As has been said, the mercury thermometer is little used at present to define the standard scale; but it can serve as a permanent sub-standard after comparison with the gas scale. As an example of this the mean 'verre dur' mercury thermometer scale is that defined by four primary standard mercury thermometers made by Tonnelet of French hard glass. These were carefully compared with the international hydrogen scale by Chappuis, observed readings of the mercury thermometers being corrected for:

1. Inequalities of the bore.
2. Effect of external pressure (variation from 76 cm.) on the bulb.
3. Effect of internal pressure (height of mercury above centre of bulb).
4. Effect of zero correction (this also corrected for 1, 2 and 3 above).
5. Error in the fundamental interval  $0^\circ$  to  $100^\circ$ .

These thermometers may be considered as the custodians, so to speak, of the international hydrogen scale.

**Measurement of Temperatures between  $100^\circ$  and  $500^\circ$  by a Mercury Thermometer.** At  $100^\circ$  the vapour pressure of mercury is 276 mm. and it boils at atmospheric pressure at  $356.7^\circ$ . It is possible to construct mercury thermometers to read to temperatures as high as  $550^\circ$  by filling the space above the mercury with a compressed gas. The gases

CORRECTION TO EXPOSURE  
 N - No. of  
 T - Temperatures observed  
 / - Temperatures on cooling Th

IN

N	$T^{\circ}, t^{\circ}$										$\theta^{\circ}$									
	10"	20"	30"	40"	50"	60"	70"	80"	90"	100"	110"	120"	130"	140"	150"	160"	170"	180"	190"	200"
100	-15	-30	-50	-60	-80	-90	-1	-1	-2	-4	-5	-7	-9	-10	-12	-15	-17	-20	-24	-30
110	-20	-30	-50	-70	-90	-100	-1	-2	-4	-5	-7	-9	-10	-12	-15	-17	-20	-24	-28	-34
120	-20	-40	-60	-80	-100	-110	-1	-3	-5	-7	-9	-10	-12	-15	-17	-20	-24	-28	-33	-37
130	-20	-40	-60	-80	-100	-110	-1	-5	-7	-9	-10	-12	-15	-17	-20	-24	-28	-34	-38	-40
140	-20	-40	-70	-90	-110	-120	-1	-6	-9	-10	-12	-15	-17	-20	-24	-28	-34	-39	-41	-43
150	-20	-50	-70	-90	-120	-130	-1	-7	-10	-12	-15	-17	-20	-24	-28	-34	-39	-42	-44	-46
160	-25	-50	-80	-100	-120	-140	-1	-8	-12	-15	-17	-20	-24	-28	-34	-39	-44	-47	-49	-49
170	-30	-50	-80	-110	-130	-150	-1	-9	-14	-17	-20	-24	-28	-34	-39	-44	-47	-50	-52	-52
180	-30	-60	-80	-110	-140	-160	-1	-10	-16	-19	-24	-28	-34	-39	-44	-49	-50	-53	-56	-55
190	-30	-60	-90	-120	-150	-180	-1	-11	-18	-22	-28	-34	-39	-44	-49	-54	-53	-56	-59	-59
200	-30	-60	-90	-120	-160	-190	-2	-12	-20	-26	-32	-37	-40	-43	-46	-49	-52	-56	-59	-62
210	-30	-70	-100	-130	-170	-200	-2	-13	-22	-30	-36	-39	-42	-45	-48	-52	-55	-58	-62	-65
220	-30	-70	-100	-140	-180	-210	-2	-14	-24	-32	-37	-41	-44	-47	-51	-54	-58	-61	-64	-68
230	-35	-70	-110	-140	-190	-220	-2	-15	-26	-35	-39	-43	-46	-49	-53	-57	-61	-64	-67	-71
240	-40	-70	-110	-150	-200	-230	-2	-16	-28	-37	-41	-45	-48	-52	-55	-59	-63	-67	-70	-74
250	-40	-80	-110	-150	-210	-240	-2	-17	-30	-40	-42	-46	-50	-54	-58	-62	-66	-70	-73	-77

used are carbon dioxide and nitrogen and the pressures twenty to thirty atmospheres; the glass must also have a high softening point, since it has to stand these pressures without deformation of the bulb. Jena borosilicate glass 59''' is satisfactory up to 500° and Jena combustion glasses will stand 580°. The capillary of these thermometers is, in manufacture, first closed at the top by a piece of fusible metal or shellac; this allows the capillary to be sealed while a high pressure is maintained within it.

Thermometers have also been constructed of silica and containing nitrogen under still greater pressure, which read up to 750°. The errors with mercury thermometers at high temperature are usually considerable, and when accuracy is the first consideration, the platinum resistance thermometer is much to be preferred.

**Accuracy attainable with a Mercury Thermometer.** The following gives some idea of the accuracy attainable in the laboratory, using a thermometer which has been compared with a standardized thermometer and to which the corrections necessary have been applied:

	Accuracy.
0–100°	$\pm 0.02^\circ$
100–200°	$\pm 0.05^\circ$
200–400°	$\pm 0.5^\circ$

Frequently, however, the precise measurement of temperatures is less important in practice than the measurement of temperature rises. With suitable precautions,<sup>1</sup> routine measurements of temperature rises can be made with an accuracy of 0.002°.

**Thermometers for Special Purposes.** For special purposes in the physico-chemical laboratory a number of modified mercury thermometers are available. For example, in large operations a thermometer with a long capillary is employed; the scale reading, say from 0° – 100°, covers only the upper portion of the capillary, so that the instrument can be used in a deep vessel. Care is needed in its use, as owing to the large amount of emergent stem definite conditions of immersion are necessary.

At the other extreme are short thermometers, in which, in order to give an open scale, without a long capillary, only a limited number of degrees appear on the scale and several such thermometers are employed for an extended range. Such thermometers are of use in avoiding an emergent thread correction, or for temperatures over 100°; a thermometer reading to 200° graduated in 0.1° is too long to be serviceable.

**Beckmann Thermometer.** The Beckmann type of thermometer, in which for greater sensitiveness only a very few degrees are included on the scale, finds application in calorimetry, and in the determination of freezing-point depressions and the like.

**Maximum and Minimum Thermometer.** Thermometers which show the highest and lowest temperatures reached during any given interval are chiefly employed in meteorology, but are also of service in practical physical chemistry. Rutherford's and Six's are the types most commonly employed.

<sup>1</sup> Sutton, *J. Sci. Inst.*, 1931, 8, 98.

**Rutherford's Maximum and Minimum Thermometer.** Rutherford's maximum thermometer is an ordinary mercury thermometer fitted with a small iron index which is pushed up by the mercury as it rises and



FIG. 11 (X)

remains in position when the mercury falls. In his minimum (Fig. 11 (X)) thermometer alcohol is the thermometric liquid and the index is of glass. It is withdrawn owing to capillarity by the alcohol as it falls, but remains stationary when the alcohol commences to rise.

**Six's Maximum and Minimum Thermometer.** In Six's thermometer (Fig. 12 (X)) a capillary bent into a U-tube terminates at each end in a bulb. The capillary contains mercury while one of the bulbs is completely and the other is partially filled with alcohol. A glass index is contained in each arm of the tube above the mercury and surrounded by alcohol.

These glass indexes are fitted with small iron wires to act as springs to keep them in position and to enable them to be moved in the tube for resetting purposes by means of a magnet. When the temperature is rising the expansion of the alcohol in the bulb causes the index (shown at 60° F. in diagram) to be pushed before the moving mercury; in a falling temperature the index (shown at 10° F. in diagram) is displaced. Each remains in position when the mercury moves away from it. Suitable scales are attached to each of the arms of the U-tube.

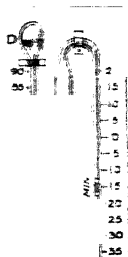


FIG. 12 (X)

**Self-recording Mercury Thermometers.** Thermocouples and the like are most usually employed when a continuous record of temperature is desired. A continuous record can also be obtained with a mercury thermometer by photographic means. A slip of sensitized paper is caused to pass at a uniform rate behind a slit in front of which is a specially designed mercury thermometer. The mercury column stops a portion of the light so that a trace of its height is recorded.

**Signalling Thermometers.** Mercury thermometers can also be employed to give warning of temperature fluctuations outside certain limits, by introducing into the capillary, platinum wires at heights corresponding to special temperatures. The rise and fall of the mercury makes and breaks electrical contact with these wires and causes any desired signals.

**Use of the Mercury Thermometer in Industry.** Owing to the simplicity with which it can be applied and read the ordinary mercury thermometer has a wide industrial use. It suffers however from the disadvantage of fragility, and further it must be read *in situ*. Mercury thermometers are consequently coming into use in which the bulb is of steel or like metal attached to a long flexible steel capillary which leads to a suitably graduated indicator (Fig. 13 (X)). Compensating devices are fitted to allow

for the large amount of 'emergent thread'. In one form of instrument a number of lengths of 'invar' are introduced into the capillary, the ratio of the diameters of which to the internal diameter of the capillary is adjusted so that the effect of change in volume of the capillary is just equal to the corresponding change in volume of the mercury filling it, whatever the temperature to which the capillary is exposed.

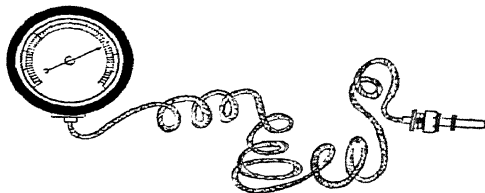


FIG. 13 (X)

**Other Mercury Thermometers.** Besides those employed in the ordinary routine of physico-chemical laboratories a great variety of other mercury thermometers designed to meet the specialized needs of other sciences are available. These include meteorological, clinical and similar thermometers, and for a description of these, appropriate text-books must be consulted.

**Advantages of Mercury as a Thermometric Liquid.** Mercury is adopted in most liquid-and-glass thermometers, owing to the following advantages which it possesses over other liquids. It exists as a liquid over a convenient and a wide range of temperature, its melting-point being  $-40^{\circ}$  and its boiling-point at 760 mm.  $356.7^{\circ}$ ; at higher pressures the boiling-point can be increased to over  $550^{\circ}$ . Its expansion is regular, it does not exhibit any abnormality such as water does at  $4^{\circ}$ , and the expansion is nearly proportional to the absolute temperature as shown by a gas thermometer. Further, mercury does not wet glass, so that it can be used in fine capillaries; it is opaque, so that a thin thread is readily seen, and it is not difficult to obtain pure. On the other hand the high specific gravity of mercury limits the size of the bulb, as the relatively large weight of the contained metal otherwise strains it, especially at high temperature.

**For Low-temperature Thermometers.** (See this chapter, S. 6.)

**High-Temperature Thermometers: Sodium-potassium Thermometer.** Attempts to replace mercury by substances with a higher boiling-point, such as tin, for work at higher temperatures with liquid-in-glass or silica thermometers, have not on the whole been successful. A thermometer has been devised in which an alloy of 4 parts of sodium and 1 part of potassium is substituted for mercury. This alloy is liquid between  $-8^{\circ}$  and  $+700^{\circ}$ . It can be used without gas filling, but it is convenient to introduce sufficient pure nitrogen to cause the internal and external pressures to be approximately equal at the higher limit temperatures so that deformation of the glass is avoided. In order that these thermometers may not be inconveniently long they are usually graduated only from  $200^{\circ}$  upwards.

**Silica Thermometers.** Transparent varieties of silica are coming into use for high-temperature thermometers to increase the available range and to avoid the troubles and changes of zero which occur in glass thermometers. Such changes are negligible with mercury-in-silica thermometers.

Unfortunately sufficiently uniform capillaries have not as yet been obtained with silica to enable such thermometers to be employed for precision work.

**Weight Thermometer.** The weight of a liquid such as mercury, which is expelled from a glass vessel completely filled at a standard temperature and heated to another unknown temperature, can be employed to determine the value of the second temperature. The weight-thermometer in which this principle is applied is described later.

### SECTION 3: PLATINUM-RESISTANCE THERMOMETERS

**Introduction.** The electrical resistance of a metallic wire is found to increase gradually with the temperature, and consequently on this property a system of thermometry may be founded. The resistance of a wire can be measured very accurately and in consequence the method gives a close measure of the actual temperature. The platinum thermometer in which this principle is practically applied was invented by Siemens, but the advantages in the use of such a thermometer were first established by Callendar and confirmed by Griffiths. They found that the resistance of pure platinum at a given temperature is always the same and is not subject to any permanent change by heating or cooling provided it is not chemically or physically altered. Further, a thermometer so constructed is easily manipulated, and when once standardized by comparison with a gas thermometer it can be used to standardize other thermometers as well as for the direct measurement of temperatures. Other metals may replace platinum, but owing to the great inertness of this substance, and its high resistance, it is more suitable than most metals.

This comparison with a gas thermometer is facilitated by the fact that the wire forming the thermometer may be enclosed in the bulb of the gas thermometer.

**The Platinum-resistance Scale.** The resistance of pure platinum increases with temperature according to the equation

$$R_t = R_0(1 + \alpha t - \beta t^2)$$

where  $R_t$  is the resistance at a temperature  $t^\circ$ ,  $R_0$  is the resistance at  $0^\circ$ , and  $\alpha$  and  $\beta$  are constants; approximately  $\alpha = 3.96 \times 10^{-3}$ ,  $\beta = 5.8 \times 10^{-7}$ . Since electrical resistances are capable of measurement with very great accuracy, this gives us an excellent means of measuring temperatures.

The platinum-resistance thermometer scale is defined by the resistance of a platinum wire thus: if  $R_0$ ,  $R_{100}$  and  $R_t$  represent the resistances at the temperatures  $0^\circ$ ,  $100^\circ$  and  $t^\circ$ , the temperature  $p_t$  is given by the relation

$$p_t = \frac{R_t - R_0}{R_{100} - R_0} \cdot 100$$

This assumes that the simple formula  $R_t = R_0(1 + \alpha t)$  is correct. The temperature so obtained consequently differs somewhat from the temperature on the international scale, but Callendar and Griffiths showed that the following equation holds:

$$T - p_t = \delta \left[ \left\{ \frac{T}{100} \right\}^2 - \left\{ \frac{T}{100} \right\} \right] = \delta \left\{ \frac{T}{100} - 1 \right\} \cdot \frac{T}{100}$$

Here  $\delta$  is a constant for a given platinum wire and varies with the degree of purity. The purity of the platinum must be such that  $\delta$  is not greater



than 1.52 and  $\frac{R_{100}}{R_0}$  is not less than 1.386. The value of  $\delta$  is determined by observations of the resistance at the temperature of melting ice ( $0^\circ$ ), at the temperature of the vapour of water boiling at normal atmospheric pressure ( $100^\circ$ ), and at the temperature of the vapour of sulphur boiling at normal atmospheric pressure in a specified form of apparatus and under specific conditions. The boiling-point of sulphur at a pressure of  $p$  mm. of mercury is related to that at N.T.P. by the formula

$$T_s = 444.5 + 0.0908(p - 760) - 0.000047(p - 760)^2$$

Ordinary commercial stock sulphur has practically the same boiling-point as pure sulphur.

**Agreement of Platinum Scale and Gas Scale.** Between  $0^\circ$  and  $100^\circ$ , the agreement between temperatures deduced from the platinum scale and those obtained from the gas scale is within the limits of experimental error. At all temperatures between the freezing-point of mercury and the boiling-point of sulphur, the agreement is sufficiently good for most scientific purposes. At temperatures above  $500^\circ$  the scale is not known with an accuracy greater than 0.5, and it becomes more uncertain as the temperature rises. For the range  $-200^\circ$  to  $1,100^\circ$ , the platinum-resistance thermometer serves as one of the most accurate and convenient means of measuring temperatures with precision. On this account the Reichsanstalt, the German N.P.L., has abandoned the gas thermometer as a fundamental experimental standard and adopted the platinum-resistance thermometer, calibrated at the ice, steam, and sulphur points and having  $R_{100}/R_0$  not less than 1.388 and  $\delta$  as limited above, as its fundamental scale for certification purposes from  $-39^\circ$  to  $455^\circ$ . This decision, however, probably flatters the resistance thermometer, since, as defined, it is not known with certainty to reproduce the international scale to within  $0.01^\circ$ .

The Callendar equation does not define a reproducible temperature below  $-40^\circ$ . Temperatures calculated from the Callendar equation are generally more than  $2^\circ$  too low at liquid-air temperature. The amount of departure from the thermodynamic scale is not the same for all thermometers. Henning has completed a correction curve and calibration table in which the resistance ratio is represented to be applied as correction to the temperature as calculated by the Callendar equation.<sup>1</sup> Van Dusen has also given a correction equation involving an additional term to the Callendar equation.<sup>2</sup> Keys, Townshend and Young<sup>3</sup> state that the deviation of a platinum resistance thermometer is to some extent dependent on the particular instrument employed. Loomis and Walters<sup>4</sup> have shown that the flat-coil calorimetric type of thermometer, when properly constructed, offers an exact means of reproducing the thermometric scale at low temperature by calibration at one low temperature point, and that their results together with those of Van Dusen established the reproducibility of pure platinum as a thermometric resistance wire when used under strain-free condition at low temperature.

<sup>1</sup> Loomis and Walters, *J. Amer. Chem. Soc.*, 1924, 47, 2852.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1925, 47, 326.

<sup>3</sup> *J. Math. Phys. Massachusetts Inst. Tech.*, 1922, 1, 243.

<sup>4</sup> *Ibid.*

**The Platinum-resistance Thermometer.** The resistance thermometer (Fig. 14 (X)) consists of a coil of pure fine wire in a porcelain, quartz, or glass sheath, which for commercial use can further be enclosed

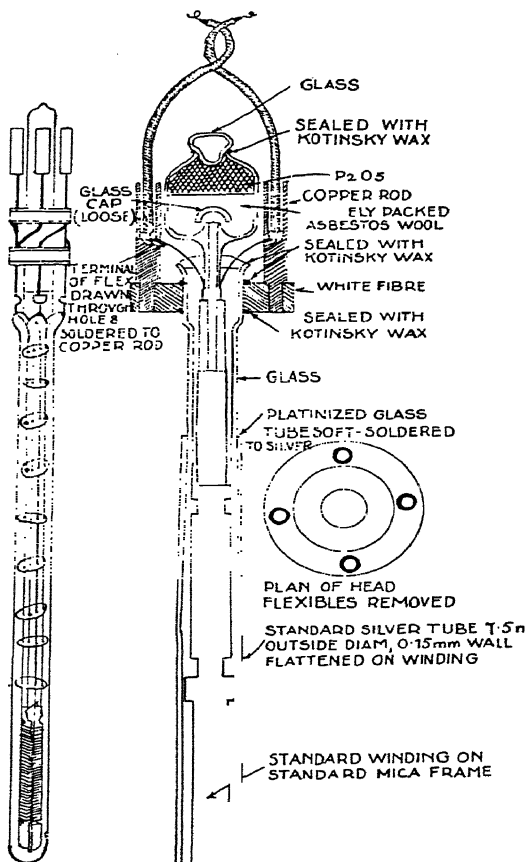


FIG. 14 (X)

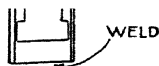


FIG. 15 (X)

in an outer removable steel tube. The wires of the coil are kept from contact by means of mica distance pieces, and the tube is sealed to prevent access of moisture; de Khotinsky cement is generally employed as

seal. In the form shown, which was developed by Callendar and Griffiths, the leads to the Wheatstone bridge used to measure the resistance were of heavy platinum wire to avoid thermoelectric effects. A similar pair of wires in the form of a loop was laid alongside and connected to the opposite arms of the bridge so as to compensate for the resistance of the leads to the coil at all temperatures. This latter principle is applied in all forms of the platinum thermometer both in academic and industrial use. The sheath employed should be as thin as possible consistent with the usage to which the thermometer is to be subjected in order to diminish time-lag in the coil assuming the temperature under investigation.

Dickinson and Mueller<sup>1</sup> have developed a type of thermometer (Fig. 15 (X)) in which a silver sheath is used and lag is thus reduced to a minimum. Instruments with a small lag are necessary in calorimetry.

**Purity of the Platinum.** Pure platinum gives a value of  $\alpha$ , the mean coefficient between 0° and 100°, as high as 0.00389 with  $\delta$  about 1.5 or slightly less. Impure wire, on the other hand, may give values of  $\alpha$  only 60 per cent of the above, and of  $\delta$  up to 1.6. Further, the zero of the instrument will not remain constant in use.

**Presence of Moisture in the Thermometer.** The presence of moisture reduces the insulation resistance between the coil and the sheath, which ordinarily should exceed 200 megohms. When this insulation is low accurate results cannot be obtained. To test for the presence of moisture a Wheatstone bridge with the thermometer in circuit is balanced by adjusting the resistance with the battery circuit closed. On opening a key in the latter circuit there is a large galvanometer deflection which gradually diminishes; on closing the key there is a large deflection in the opposite direction, which slowly vanishes as the circuit is kept closed. This phenomenon is distinguished from that due to the use of an excessive measuring current by the absence of the galvanometer deflection in the latter case when the battery circuit is opened.

**Resistance Bridge.** To determine the resistance which measures the temperature, the coil of wire constituting the thermometer is made one arm (D) of a Wheatstone bridge (Fig. 16 (X)), the other three arms, A, B, C, being formed from material the resistance of which does not change with temperature. Current is supplied to the bridge by an accumulator E or other suitable means. To eliminate thermo-electric effects a reversing key K is provided. If the resistances of the four arms are in the ratio  $a/b = c/d$ , no current will flow through the galvanometer G, which serves as the temperature indicator. The energy consumed in such a circuit is very small and the 2-volt or 4-volt accumulator will only need recharging at long intervals. The manipulation of the variable resistances and of the battery and galvanometer keys is the same as with the Post Office box or the like.

In order that compensation for the resistance of the leads may readily be accomplished by the provision of a second pair of leads, the bridge employed must have equal ratio arms  $a$  and  $b$ . Further, it must be so arranged that it is capable of measuring changes of resistance to a high order

<sup>1</sup> *Phys. Rev.*, 1907, 24, 529; *J. Amer. Chem. Soc.*, 1907, 29, 1381; *Bur. Standards Bull.*, 1913, 9, 483.

of accuracy. For example, if the platinum wire employed has a resistance of 2.5 ohms at  $0^{\circ}$  it will have an increase of resistance of about 1 ohm when heated to  $100^{\circ}$ , so that to determine  $0.01^{\circ}$  necessitates resistance measurements of the order  $10^{-4}$  ohms.

In practice this is accomplished by balancing the arm C to the nearest 0.05 ohm with the aid of coils inserted by means of plugs or dials in the usual way, and then obtaining the final adjustment, using a bridge wire or a set of shunted coils. It is to be observed that the absolute values of the coils used are not of importance provided the relative values are accurately known.

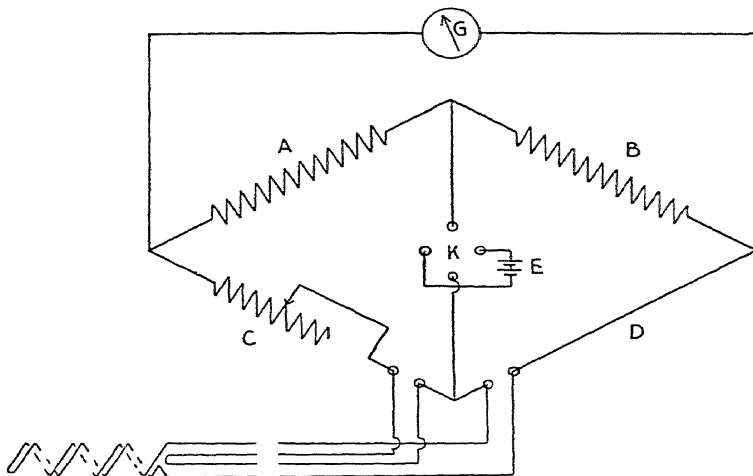


FIG. 16 (X)

**Temperature Control.** Owing to the variation of resistance with temperature it is necessary to know the temperature of the bridge resistance. With manganin coils of good quality the variation in resistance with temperature is very small. Accuracy to 1 part in 25,000 can be achieved if the coil temperatures are known to  $2^{\circ}$ . For greater accuracy the whole apparatus is immersed in a thermostat containing oil.

Manganin has the further advantage that it has a very small thermal E.M.F. against copper, which is frequently used for the leads. It is, however, subject to gradual changes in resistance, so that the coils need calibration from time to time. It is advisable to have all the coils except the bridge wire in cases sealed with moisture-free paraffin to eliminate disturbing effects due to adsorbed moisture.

**Heating Effect of Current Employed on Thermometer Coil.** A convenient size for the thermometer coil and a reduction of the thermometric lag to the minimum is obtained by employing platinum wire of about 0.2 mm. in diameter. This renders the heating effect of the current employed, which is usually about 0.01 amp., not entirely negligible; it is of the order of  $0.01^{\circ}$ . The bridge coils are sufficiently heavy and well cooled for the heating effect with them to be ignored.

At various temperatures the net heating effect of the same current will vary owing to the radiation losses from the wire increasing with the temperature, and the precise laws which govern the phenomena are unknown. Nevertheless, sufficiently accurate results are obtained by keeping the total resistance of the thermometric circuit constant and applying the following empirical rule given by Callendar: Take away one-third the difference in reading when the battery consists of two secondary cells in series from the reading when in parallel. To maintain the resistance of the thermometric circuit constant in order to have a constant current with a constant E.M.F., a variable resistance is employed in series with the battery. Alternatively, a variable resistance of the plug or dial type is inserted in the arm of the Wheatstone bridge containing the thermometer coil, and this is adjusted as the resistance of the thermometer coil changes, so that the total resistance in that arm remains constant; the value of the adjustment gives the change in resistance of the thermometer coil and hence the temperature.

**Whipple Indicator.** Although in the laboratory more or less complicated resistance boxes are used to contain the balancing coils, for industrial use a more robust instrument is required. This is provided by the Whipple indicator in which the resistance box is replaced by a long bridge wire wound spirally on a drum. A sensitive galvanometer is pivoted at the top of the case and balance obtained by rotating the drum. Readings can be obtained to about  $0.3^{\circ}$  at  $1,100^{\circ}$ .

## SECTION 4: THERMOCOUPLES

**Introduction.** If two wires composed of dissimilar metals are joined at their ends to form a closed circuit and one of the junctions is heated, a current will pass in the circuit and it is found that the magnitude of the small electromotive generating this current is proportional to the difference in the temperature of the hot and cold junctions. Consequently, if a sensitive voltmeter is introduced into the circuit and the cold junction is maintained at a constant temperature the readings of the voltmeter can be employed to determine the temperature of the heated junction.

**Simple Thermoelectric Circuit.** Fig. 17 (X) shows a simple thermoelectric circuit in which E is the hot junction, F the cold junction, and A the temperature indicator. C and D are dissimilar metals joined to the voltmeter by copper leads B. A millivoltmeter serves as a temperature indicator; if desired, it can be graduated directly in  $^{\circ}\text{C}$ . The temperature of the pair of points  $a$  and  $b$ , and in fact of all pairs of points at which dissimilar metals are joined, e.g.  $c$  and  $d$ , must be maintained equal in order



FIG. 17 (X)

to prevent the generation of effective thermoelectric E.M.F.s other than that under observation.

If desired the strip of metal  $Fb$  can be omitted and the wire  $EF$  connected directly to the copper lead at  $b$ , when if  $a$  and  $b$  are maintained at the temperature of the cold junction  $F$ , the correct reading at  $A$  for a given temperature at  $E$  is obtained. This follows from the fact that if the thermoelectric E.M.F.s generated in circuits composed of two metals  $A$  and  $B$  respectively and a third metal  $C$ , by unit difference in temperature between the hot and cold junctions, are known, the thermoelectric E.M.F. produced in a circuit composed of  $A$  and  $B$  for unit difference in temperature is the algebraic difference of the two quantities.

**Use of Thermocouples.** Thermocouples are not used to define a temperature scale, since it is found that the temperature-electromotive force relations which have been worked out empirically will not bear extra-

polarization over long intervals. The couple is calibrated by actual experiment, using substances of known boiling- or freezing-point, such as are listed in the fixed-point scale (see this chapter, S. 1). Conversely, thermocouples are often employed to transfer from the gas scale to the fixed-point scale, and thus determine points on the latter.

Thermocouples can be used to measure temperatures from  $1,500^{\circ}$  to  $-200^{\circ}$ , with a degree of precision second only to that of the platinum-resistance thermometer; in fact, above  $1,100^{\circ}$  the thermoelectric is the only convenient and sensitive electrical method available. At low temperatures it is rather insensitive.

It is to be noted that the wires forming the couple need not necessarily be pure metals; one or both can be and often are composed of alloys of various types.

**Selection of Suitable Materials for a Thermocouple.** In selecting suitable materials for the thermocouple, attention has to be paid to the following points:

(1) Non-homogeneity due to variation in composition of the wires, or produced by the heating itself. With some materials the effect is so large as to make them quite useless for the purpose.

(2) Annealing. This is essential to get rid of the cause of thermoelectric effects due to some parts of the wire being hardened during the construction of the couple. Platinum wires are, for example, annealed in an electric furnace at  $1,400^{\circ}$ .

(3) Constancy of the wires under the conditions of use.

(4) Melting-point.

Platinum and platinum with 10 per cent of rhodium form the most suitable couple: platinum and platinum-iridium are also good, in so far as freedom from parasitic currents is concerned, but do not stand high temperatures quite so well. A reducing atmosphere and the vapours of metals, such as copper, zinc, silver, &c., attack platinum and its alloys very rapidly, and protection from these must therefore be provided. Furthermore, at very high temperatures, it is impossible to prevent volatilization of rhodium or iridium from the alloy limb to the pure platinum limb.

**Construction of Couple.** The diameter of the wire is usually 0.6 mm. to give robustness; a larger diameter leads to too great heat conduction with consequent cooling of the junction. Before using wires for the construction of apparatus for accurate work, they must be tested for homogeneity. This can be done by connecting each wire in turn by copper leads to a sensitive galvanometer calibrated in microvolts; the junctions at the end of the wire are both kept at  $0^{\circ}$ , and the wire is passed through a short electric furnace at  $1,000^{\circ}$ , or through a porcelain tube heated by a Bunsen burner. The furnace is moved along the wire and readings taken of the E.M.F. with the furnace at various points. With some wires, irregularities amounting to 300 microvolts and equivalent to a temperature error of  $30^{\circ}$  are found, while with good material they will be less than 10 microvolts.

The ends of the two wires should be connected by autogenous welding; this can be carried out by twisting them together for the last 5 mm. and supporting the junction in front of an oxyhydrogen burner; the oxygen is turned on first and then the hydrogen is gradually increased till the end

of the junction melts and is then immediately stopped. The wires are next annealed to make them as homogeneous as possible, by passing a current large enough to make them glow strongly, when any lack of homogeneity can generally be observed. The two wires are insulated from one another by threading on them mica washers and short lengths of thin tubes made of hard porcelain (Fig. 18 (X)) with mica supports, and are then protected by pushing the junction to the bottom of a porcelain tube.



**Measurement of E.M.F.** Two methods of measuring the E.M.F. are in use: (1) the potentiometer, which gives direct measurements and is always employed for precision work; (2) some form of high-resistance galvanometer is calibrated to read millivolts or  $^{\circ}\text{C}$ . This latter is very convenient for technical purposes, but is less accurate. The principle of the potentiometer method is illustrated in the diagram (Fig. 19 (X)). A battery of storage cells A is connected through a variable resistance R to the ends of a uniform wire which extends from the resistance to  $S_1$  and a constant drop in potential is maintained over this wire, the potential difference between any two points on the wire is then proportional to the distance  $l$  between the points. To check the constant potential difference a standard cadmium cell (E.M.F. = E) is connected to the galvanometer G, and the potential difference of its terminals kept in balance against that, along a length of the wire  $l$ ; then the E.M.F.  $E_1$  in the thermocouple circuit  $e$  can be balanced against a length  $l'$ . Then  $E/E_1 = l/l'$ , or  $E_1 = E \cdot l'/l$ .



FIG. 18 (X)

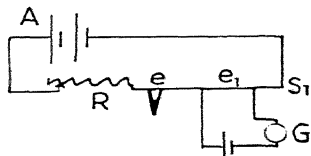


FIG. 19 (X)

**Potentiometer for Accurate Work.** In the Cambridge Scientific Company's potentiometer for use with thermocouples, the arrangements are as shown in Fig. 20 (X). The range is 30 millivolts and readings can be obtained by estimation to 1 microvolt, equivalent to  $0.1^{\circ}$  at  $1,000^{\circ}$ , with platinum-platinum rhodium couples.

The battery circuit is shown by dotted lines, the battery being connected at  $ab$ ;  $ss$  is the portion of the slide-wire for balancing the E.M.F. of the standard cell connected at  $cd$ ; while another portion of the wire ending at V is used for balancing the E.M.F. of the thermocouple connected at X. The switch K enables the galvanometer to be connected to either the standard cell or the thermocouple circuit.

Resistance A is about 42.5 ohms and B about 51 ohms, so as to give a potential difference between a point M (not shown) and the point N (on the slide-wire  $ss$ ) approximately equal to the E.M.F. of the cadmium cell. N is set so that the scale gives directly the reading corresponding to the known E.M.F. of the cell and the potential between M and N is altered by means of the resistances  $R_2$  until it is just sufficient to balance that of the cell; when this balance is obtained the galvanometer will show no current when the galvanometer key K is depressed. The E.M.F. of a



cadmium cell at  $20^\circ$  is  $1.0183 \pm 0.0005$  international volts (the exact value can be obtained by having it standardized at the N.P.L.) and the temperature effect is given by the equation

$$E_t - E_{20} = 0.0000406(t - 20) - 9.5 \times 10^{-7}(t - 20)^2$$

The resistances of the various parts of the circuit are so proportioned that when the potential difference between M and N is equal to that of the cell, it is equal to about 1 volt per 50 ohms, so that 0.05 ohm equals 0.001 millivolt. The dial P, which is used with  $vr_1$  to balance the E.M.F. of the thermocouple, has twenty-nine coils, each of 0.05 ohm resistance, so as to enable one to balance whole numbers of millivolts between 0 and 29.

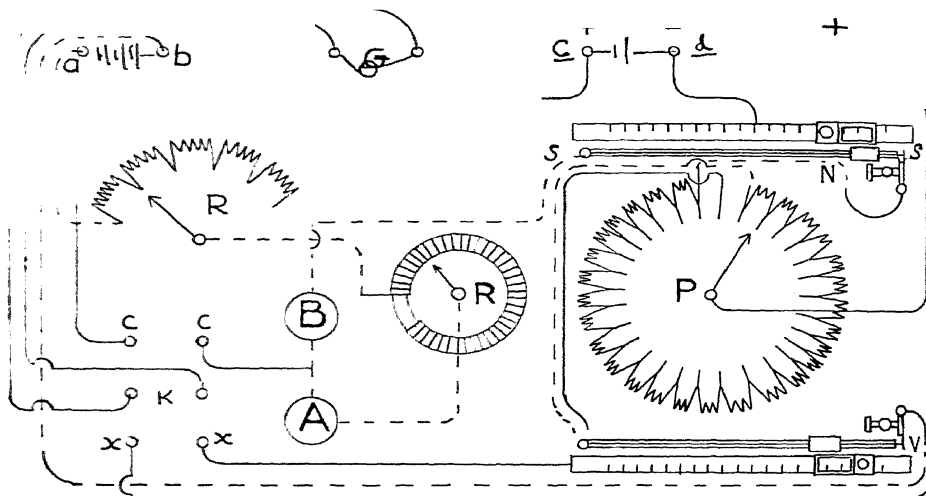


FIG. 20 (X)

The slide-wire  $vr_1$  has a resistance of 0.06 ohm and a total potential difference of 1.2 millivolts; 30.2 millivolts is thus the maximum measurable potential difference. This is ample for the range of temperature over which thermocouples can be used.

All the coils are of manganin to avoid any temperature coefficient of resistance, and all connexions are copper to minimize risk of contact E.M.F.s. A constant battery E.M.F. is always essential; this can be secured by using accumulator cells of large capacity or several cells joined in parallel and maintained at a fairly constant temperature. It is most important to prevent leakage from one part of the circuit to another and from outside; the latter can be attained by using an equipotential shield made of metal and on which all the measuring apparatus is placed.

**Galvanometer Method: Effect of Couple Temperature.** The galvanometer method is extremely convenient for giving approximate temperatures. The galvanometer measures current and this is proportionate to the E.M.F. as long as the resistance remains constant. The

resistance of the thermocouple itself depends upon the temperature and is therefore not constant, while the galvanometer is not subjected to more than small temperature changes, so that its resistance only varies to a small extent. This invariable resistance must therefore be high in comparison with the variable couple resistance, if the whole is to be sensibly invariable, so that a high-resistance galvanometer must be used. The ordinary platinum-platinum rhodium thermocouple has a resistance of about 2 ohms when cold and 4 ohms at  $1,000^{\circ}$ ; the galvanometer has a resistance of 200 ohms, the resistance of the circuit when cold is 202 ohms, and when the whole of the thermocouple is at  $1,000^{\circ}$  204 ohms, giving an error of 1 in 100, equivalent to about  $10^{\circ}$ . In practice, the whole of the couple is not immersed, and only part of it is at  $1,000^{\circ}$ , so that the error is less, but it is dependent on the depth of immersion and this prevents precise measurements. With base metal couples the resistance may be as low as 0.1 ohms and a galvanometer of only 10 ohms resistance would not give a greater error than in the above case.

**Effect of Galvanometer Temperature.** The temperature of the galvanometer and of the copper leads, when the latter are long, may be of considerable importance. For example, if the temperature coefficient of the galvanometer is 0.1 per cent per degree we have the same percentage error in the temperature indicated for each degree of difference between

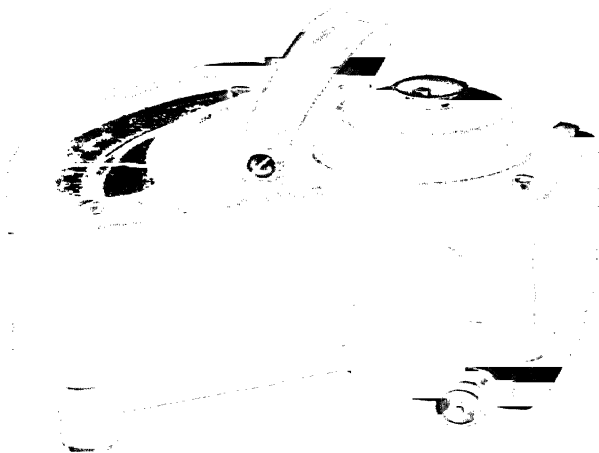


FIG. 21 (X)

the temperature at which the galvanometer is used, and that at which it was calibrated.

Galvanometers (Fig. 21 (X)) suitable for use with thermocouples can now be obtained with a total resistance of 100 ohms and a temperature coefficient of about 0.05 ohm per degree. They are robust and are not affected by external magnetic fields; nor do they change with time nor require accurate levelling. A screw locks the pointer when the instrument is to be moved and another screw on the outside of the case adjusts the

## SECTION 5: RADIATION METHODS

**Introduction.** The intensity of the light emitted by a hot body increases very rapidly with the temperature. At 2,000° the intensity of the red light emitted by a body is over 2,100 times as great as at 1,000°. Radiation methods are therefore particularly suitable for very high temperature measurements, but they have one great drawback; different substances have very different emissive powers, so that two bodies, such as carbon and polished platinum, when both at the same temperature, give very different intensities of radiation; at 1,500° this would lead to the temperature of the carbon being estimated to be 100° above that of platinum.

**Ideal 'Black Body'.** The conception of an ideal 'black body', due to Kirchhoff as being one which absorbs all the radiation which falls upon it and does not reflect or transmit any, is practically realized by a hollow opaque enclosure, the walls of which are heated as uniformly as possible, the radiation being observed through a small hole in the wall.

By the use of electrically heated furnaces with a proper distribution of the heating coils, very good results have been obtained in the construction of black bodies for the calibration of optical and radiation pyrometers. By the black-body temperature is meant the temperature indicated by a pyrometer which has been calibrated against a black body of the kind described; the black-body temperature will always be below the true temperature, often by a very considerable amount, and to get the true temperature, a correction factor has to be employed. In many practical operations, however, the black-body temperature alone is of very great value; for example, in reproducing given temperature conditions; while the interior of many furnaces, etc., gives radiation which approximates very closely to black-body radiation.

**Radiation Laws.** The following is a short summary of the radiation laws, on which is based the use of radiation measurements to measure temperature. Kirchhoff's law states that the ratio of emission to absorption for all bodies is the same function of the wave-length of the radiation and the absolute temperature, and is equal to the emission for a black body

$$e/a = F(\lambda, T)$$

From this it follows that if two different surfaces at the same temperature radiate only to each other, the radiation of each is equivalent to that of a black body. This is important as defining the condition in an enclosed space at uniform temperature and the practical realization of the black body.

**The Stefan-Boltzmann Law.** The Stefan-Boltzmann radiation law, first stated by Stefan and deduced thermodynamically by Boltzmann, states that the total energy radiated by a black body per unit area per

unit time is proportional to the difference of the fourth powers of the absolute temperatures of the body and its surroundings, that is

$$E = \sigma(T^4 - T_0^4),$$

where  $\sigma$  is a constant,  $T_0$  is the temperature of the body on the absolute scale which receives the radiation; at high temperatures  $T_0^4$  is negligible compared to  $T^4$  and  $E = \sigma T^4$ .

The value of  $\sigma$  is  $1.279 \times 10^{-12}$  and equals the radiation per degree Centigrade per square centimetre expressed in gram calories per second. The law is only true for black bodies; for other substances the value of  $\sigma$  increases with temperature, but the total energy in these cases may be represented by  $E = \sigma_1 T^{(a-1)}$ , where ' $a$ ' has a value between 5 and 6.

**Wien's Laws.** As the temperature of a body is increased, so it gives out energy of shorter wave-length; the energy of all the wave-lengths in the energy emitted increases with temperature, but the wave-length of maximum energy becomes displaced towards shorter wave-lengths.

Wien's displacement law applied to black bodies states that the wave-length of maximum energy multiplied by the absolute temperature is a constant, i.e.  $\lambda_{\max} T = \text{constant} = A = 2,920$ , where  $\lambda_{\max}$  is the wave-length of maximum energy in centimetres, and  $T$  is the absolute temperature in degrees.

For other than black bodies the law is true but the constant has a different value; combining this law with the Stefan-Boltzmann law  $I_{\max} T^{-5} = \text{constant} = B = 2,190 \times 10^{-17}$ , where  $I_{\max}$  is the energy corresponding to the wave-length of maximum energy. These laws agree very well with experiment.

For non-black bodies  $I_{\max} T^{-a} = B'$ , where ' $a$ ' lies between 5 and 6. Wien's third law refers to radiation of any wave-length, but does not agree with experiment for long waves. It states that

$$I = c_1 \lambda^{-5} \varepsilon \frac{c_2}{\lambda T}$$

Here  $I$  is the energy corresponding to any wave-length  $\lambda$ ,  $\varepsilon$  is the base of the natural system of logarithms,  $c_1$  and  $c_2$  are constants of which  $c_2 = 5\lambda_m T = 14,500$ .

Planck deduced an expression which is more satisfactory in theory and in practice,

$$I = C_1 \lambda^{-5} \frac{c_2}{(\varepsilon^{\lambda T} - 1)^{-1}}$$

where  $C_1 = 4.965 \lambda_m T$ .

For non-black bodies the expression becomes

$$I = C_1 \lambda^{-a} \frac{c_2}{(\varepsilon^{\lambda T} - 1)^{-1}}$$

where ' $a$ ', as before, lies between 5 and 6.

**Féry Telescope.** As examples of radiation pyrometers we may take the Féry telescope and absorption pyrometers. The former instrument (Fig. 23 (X)) makes use of the Stefan-Boltzmann law

$$E = \sigma(T^4 - T_0^4)$$

The radiation from the hot body falls on a concave gold-on-glass mirror which can be adjusted by a rack and pinion so as to produce an image on a very sensitive thermocouple, thus raising the temperature of the latter and setting up an E.M.F. which serves to measure the radiation and so the temperature. The thermocouple consists of small copper and constantan wires in the form of a cross. These wires are joined to two brass strips D and R, which are attached to the terminals  $bb'$ . Two small mirrors placed close to the couple reflect the image to the eyepiece O; the mirrors are so arranged that the image appears to be split into two parts which only coincide when the focusing is correct. It is essential that the image should overlap the blackened

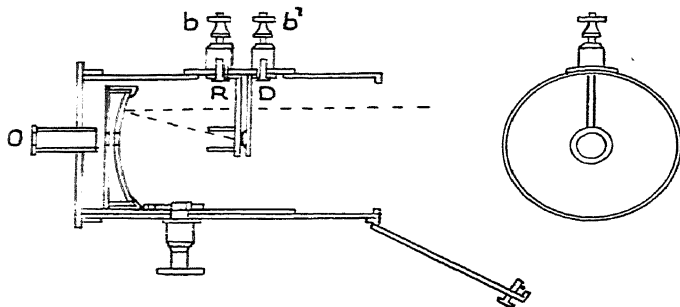


FIG. 23 (X)

silver disc which is soldered to the thermojunction, and if this condition is fulfilled the distance of the instrument from the hot body is immaterial: a diameter of the hot body of 2.5 cm. per metre distance of the instrument is required. For very high temperatures an adjustable diaphragm is provided which cuts out a definite fraction of the radiation. A direct-reading galvanometer with two Centigrade scales ( $600^{\circ}$  to  $1,300^{\circ}$ , and  $1,000^{\circ}$  to  $2,000^{\circ}$ ) or a recorder can be used. For scientific purposes a low-range potentiometer gives good results, and since  $T = k \cdot e^2$  where  $e$  is the E.M.F., plotting  $\log T$  against  $\log e$  gives a straight line, so that only two points are necessary for calibration. This form of pyrometer is of little use with molten metals owing to the effects of haze and reflected radiation from the walls of the furnace.

**Féry's Absorption Pyrometer.** Féry's optical pyrometer (Fig. 24 (X)) makes use of the light waves of one particular colour, usually red, instead of the total radiation; it can be used to measure the temperature of very small objects, such as electric-light filaments. It consists of a telescope which carries a small comparison lamp attached laterally. The image of the flame of this lamp is reflected by a mirror inclined at  $45^{\circ}$  and placed at the principal focus of the telescope, the mirror being silvered only over a narrow vertical strip. A pair of absorbing wedges are placed in front of the objective of the telescope and can be moved laterally by means of a micrometer screw until the light from the hot body appears to be of the same intensity as that from the lamp; a monochromatic glass in

the ocular only allowing light of one wave-length, e.g. red =  $6,590 \text{ \AA}$ , to pass through. For very high temperatures additional absorbing glasses can be placed in front of the wedges. The flame of the comparison lamp, which burns gasoline, is adjusted to a fixed height, and can be used after it has been burning for about 15 minutes. No correction is required for focusing or for distance from the hot body, since the angular aperture is fixed. If  $x$  is the thickness of the wedges as read from the micrometer scale  $I = ce^{kx}$ , where  $k$  is the absorption coefficient of the wedges and  $c$  is a constant. Wien's law gives  $I = Ae^{-B/T}$ , hence  $ce^{kx} = Ae^{-B/T}$  and  $kx + C = -B/T$ , the absolute temperature is therefore inversely proportional to the thickness of the wedges, so that calibration at two temperatures fixes the scale. As a standard of intensity the Hefner amyl acetate lamp may be taken as unity; the small central area of this flame gives an easily reproducible and accurate standard. A black body can

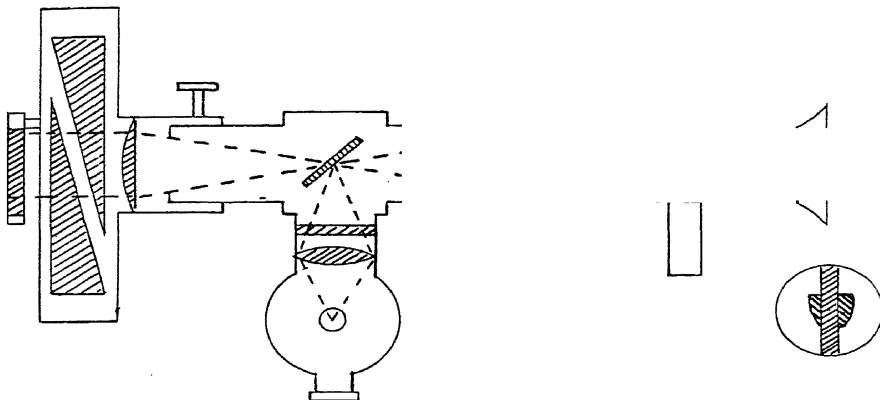


FIG. 24 (X)

be compared with this at several temperatures and the Hefner lamp then serves as a standard from which black-body temperatures can be obtained. The radiation scale extends the absolute scale to the highest temperatures known, but the degree of accuracy of the temperature measurements is at present very uncertain owing to the uncertainty of the values to be assigned to the constants  $\sigma$  and  $c_2$  in the radiation laws.

Schmidt and Furthmann<sup>1</sup> have made an experimental study of the absorption and reflection of lenses made of fluorite, quartz and glass in measuring the total radiation and the temperature of non-black bodies (e.g. polished platinum) by means of a total radiation pyrometer. Lens pyrometers are not suitable for the determination of total radiation. The temperature readings, however, of these instruments, when calibrated for a black body approach the temperature of the non-black body more closely the nearer the limit of the ultra-red absorption of the lens lies to the visible region of the spectrum. Hence a glass lens pyrometer is more suitable than a fluorite lens.

<sup>1</sup> *Mitt Kaiser Wilhelm Inst. Eisenforsch.*, 1926, 8, 103-15.

**Vapour-pressure Thermometer.** The vapour pressure of a liquid in equilibrium with its own vapour depends only on the temperature, and hence can be applied to determine the latter. Not many investigations on the method are extant; the most important is that of Stock and Nielsen, who used oxygen as the thermometric substance, and developed a thermometer suitable for use between  $-183^{\circ}$  and  $-200^{\circ}$ .

Their apparatus consists of a narrow capillary containing oxygen which is immersed in the space the temperature of which is under observation. The capillary is directly connected to a mercury manometer which can be graduated in  $^{\circ}\text{C}$ .

The instrument is very convenient in use as the vessel containing the liquid oxygen is small and the vapour pressure of oxygen is very sensitive to changes in temperature. It has, however, the disadvantage of being available only over the small range between the melting-point and boiling-point of oxygen. This disadvantage can be obviated by using other thermometric substances, such as carbon disulphide, carbon dioxide, nitrogen, &c. Except for low-temperature work the method has as yet found little application.

**Other Methods of Measuring Temperatures.** Any property of a substance or mixture of substances of which the variation with temperature can be determined readily and accurately, can be employed to measure temperature. For example, the vapour density of a substance such as mercury, the heat given out by a substance of known specific heat when cooled from the required temperature to a known one, the expansion of a solid, or alternatively the curvature of a bar composed of strips of two metals with different coefficients of expansion, the refractivity of a gas, or its viscosity, the change in E.M.F. of a standard cell with temperature, can all be made to provide thermometers.

Further, the method on which the fixed-point scale depends can also be applied to a continuous range of temperatures by employing, for example, mixtures of two components, such as water and glycerine for low temperatures, and alloys of various kinds for higher temperatures. This method is of importance industrially in controlling the temperature of pottery kilns, where small cones which melt at definite temperatures are used, e.g. Seger cones which can be supplied of different 'falling-over' points and give temperatures within small ranges.

None of these methods, however, have as yet attained any physico-chemical importance. Most of them are unsuited for giving a continuous record of temperature, such as is readily possible with the platinum-resistance thermometer and the thermocouple; it is this property which is one of the great advantages of electrical methods.

## SECTION 6: LOW-TEMPERATURE MEASUREMENT

**Low-temperature Thermometers.** For temperatures below the freezing-point of mercury other liquids can be used in thermometers similar to those described earlier. Alcohol, melting-point  $-112^{\circ}$ , is often employed, but owing to its low boiling-point,  $79^{\circ}$ , it cannot be standardized by a steam-point determination. Toluene, melting-point  $-80^{\circ}$ , boiling-point  $111^{\circ}$ , is consequently more suitable. The alcohol and toluene thermometers have been compared with the gas thermometer, and it has been found that toluene gives more regular results. These and other organic liquids such as ether, chloroform, petroleum ether (melting-point  $-188^{\circ}$ ), all have the advantages of a large coefficient of expansion.

When volatile liquids are employed, the whole thermometer should be at the temperature under observation, to prevent distillation of the liquid into the top of the capillary.

**Pentane Thermometer.** Thermometers filled with commercial liquid pentane are coming increasingly into use owing to the low melting-point of that hydrocarbon, which enables the thermometers to be used at the temperature of liquid air. At these temperatures, however, the liquid is somewhat viscous and care must be taken that in the cooling none adheres to the walls of the capillary. The instrument can be calibrated by immersion in a mixture of excess of solid carbon dioxide and absolute alcohol which has a temperature of  $-78.2^{\circ}$  at standard pressure; other points are determined by interpolation and extrapolation of the interval 0 to  $-78.2^{\circ}$ ; it is necessary for this that the capillary employed has a uniform bore.

The low boiling-point of pentane,  $25-30^{\circ}$ , is a disadvantage, as it renders it impossible to free the thermometer from air. Any gas bubbles which form in the liquid when in use must be driven into the upper portion of the capillary by heating.

Absolute zero on the ideal gas scale and on the thermodynamic scale works out at  $-273.16^{\circ}$ . There is no single method of measurement capable of covering this range.<sup>1</sup>

Measurements are usually made with suitable 'secondary' thermometers which have been calibrated against a normal helium gas thermometer, all the usual gas thermometer corrections being taken into account, and the gas scale reduced to the absolute or thermodynamic scale by applying a knowledge of the equation of state for helium.

The helium thermometer is usually the constant volume type, filled with helium at a pressure of 1,000 mm. of mercury at  $0^{\circ}$ . This normal helium thermometer is available as far down as  $-270^{\circ}$ . For lower measurements, the gas pressure (measured at  $0^{\circ}$ ) must be reduced to a few milli-

<sup>1</sup> D. J. Williams, *School Science Review*, 1937, xix, 41-2.



metres, when the pressure at a temperature below  $-270^{\circ}$  is so small that only a Pirani or a hot wire manometer can be used, and the sensitivity suffers.

Secondary thermometers include resistance thermometers, thermocouples and vapour pressure thermometers. The platinum-resistance thermometer is satisfactory as far down as  $-258^{\circ}$ , though it should be understood there is no simple relationship which describes the behaviour of the resistance at temperatures below  $-200^{\circ}$ . The thermometer has to be calibrated at many points against the gas scale.

At helium temperatures, alloys which, at ordinary temperatures, have a constant resistance, for instance, constantan, manganin and phosphor bronze, are found useful. The resistance of phosphor bronze from  $5^{\circ}$  K. to  $1^{\circ}$  K. is almost exactly proportional to the absolute temperature. Thermocouples of copper-constantan can be used down to  $-258^{\circ}$ , but gold-silver couples are more sensitive.

The use of vapour pressure determinations for temperature measurement is an old device having the advantage of great sensitivity. For instance, the vapour pressure of oxygen, near its boiling-point, changes by 80 mm. of mercury for a temperature change of  $1^{\circ}$ , whereas the pressure of an ordinary gas thermometer would change by only 4 mm.

Until recently, temperatures below  $1.47^{\circ}$  K. could be measured only by using the helium vapour pressure thermometer, the exact temperature being obtained by extrapolation. The vapour pressure of helium was measured by gas thermometers as far down as possible, and the extrapolation performed by analogy with the vapour pressure curve of hydrogen, using the law of corresponding states.

The modern work on the variation of resistance with temperature, discussed in the second part of this article, has made possible the use of resistance thermometers of suitable alloys even for temperatures in the neighbourhood of  $1^{\circ}$  K.

But the most important step in low temperature measurement is a by-product of the magnetic method of cooling, which is, in a sense, self-measuring.

According to the Curie Law, the magnetic susceptibility of paramagnetic salts of the iron and rare earth groups is approximately inversely proportional to the absolute temperature, and, generally, independent of the field strength. When, therefore, a paramagnetic salt has been cooled by adiabatic demagnetization, a determination of its susceptibility will give its temperature.

The susceptibility can be measured by bringing two coils near the apparatus, sending an alternating current through the primary, and amplifying and measuring the secondary current, which will depend on the susceptibility. Since the latter is large at very low temperatures, a high degree of accuracy is to be expected.

But de Haas used the cooling apparatus itself for gauging the temperature. He determined the susceptibility by observing the mechanical force exerted on the cooled paramagnetic salt by the small magnetic field which remained after the current in the electro magnet had been switched off. In this sense, the process was self-measuring.

Independent confirmation of these extreme temperatures is hard to obtain, but Simon has made observations on the heating effect of  $\gamma$ -ray bombardment on various substances, and asserts that magnetic temperatures, at least as far down as  $0.08^{\circ}\text{K.}$ , agree with the thermodynamic scale within 10 per cent.



## CHAPTER XI

### THERMOCHEMISTRY

#### SECTION 1: THERMAL MEASUREMENTS

**C**HEMICAL reactions, changes in structure, changes in state, &c., are nearly always accompanied by thermal effects. The measurement of such thermal changes often affords valuable evidence concerning the nature of the reaction ; in many cases no other method of following the change is known. The general method of measuring the heat evolution or absorption is to determine the temperature change produced in a known mass of substance of known specific heat. The thermal change is usually calculated for 1 gram-equivalent or 1 gram molecule of the substance or substances under experiment.

**Units.** The standard unit in thermal work is the calorie. This is defined as the amount of heat required to raise 1 gram of water from 15°–16°. The standard temperature is necessary, as the amount of heat varies slightly over the temperature scale ; this variation is neglected in ordinary thermal work. This unit is usually written *cal*. A larger unit, also much used, is written *K*. This is the amount of heat required to raise the temperature of 1 gram of water from 0–100°. It may be reckoned as 100 calories. A still larger unit, the large calorie, written *Cal*., is also used and equals 1,000 calories. The British Thermal Unit (1 lb. 1° F.) is equivalent to 252 calories.

**The Calorimeter.** Thermal measurements are carried out in an apparatus known as a *calorimeter*. This term may be taken to include not only the vessel in which the reaction takes place, but the surrounding vessels, &c., which prevent rapid thermal intercourse with the atmosphere. The success of any thermal measurement depends on the perfection of the calorimeter. The calorimeter may be elaborated according to the degree of accuracy required or the special need of the experiment.

The usual calorimeter consists of a double-walled outer vessel (Fig. 1 (XI) ) made of polished copper, which is fitted with a movable cover. The space between the walls of the vessel is filled with water. Standing inside, supported on pointed wooden blocks or corks (not shown in diagram) is a cylindrical vessel, made of polished or silvered copper. This is insulated from the outer vessel at the sides also by means of similar corks or blocks. Inside this vessel fits the reaction vessel itself, similarly insulated. This vessel is usually made of silver, gold-plated inside, or of copper, nickel, or aluminium. Its capacity varies, being usually of the order of 500 ml. It is provided with a stirrer of the same metal as the vessel, and the lids of all the vessels are bored to fit a thermometer. A stirrer is also provided

for the liquid in the double-walled vessel and its outside surface is covered with a thick layer of felt. The wall of the reaction vessel is well polished to minimize radiation. The reacting substances in a calorimeter of this type are tolerably well protected from external heat influences. Absolute heat insulation is, however, impossible, so a correction for heat losses must be applied. The method of doing this is described later. Agitation of the working liquid during the experiment is essential. Various types of stirrer may be used: stirrers mechanically driven are to be preferred to hand-worked ones: the calorimeter in some cases is designed to provide for this. In one form of instrument a screw is employed for stirring the contents. The vessel is made with an  $\infty$ -shaped cross-section, the stirrer being contained in a tube which is connected with the main tube at the top and bottom. By this method it is possible to obtain a steady circulation of

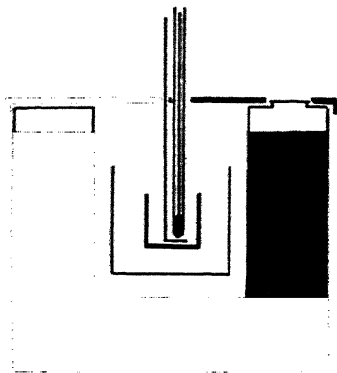


FIG. 1 (XI)

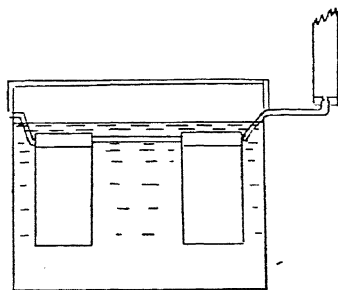


FIG. 2 (XI)

liquid through the calorimeter. This screw-propeller type of stirrer is found to be very satisfactory. The propeller may be driven by a belt connected with a small electric motor. Another common type of stirrer is an annular metal ring fitting loosely inside the calorimeter and oscillated up and down by a rod. This form is not so commendable as the other, for as the stem moves in and out of the liquid it promotes evaporation of the liquid. A paddle stirrer of the type shown in Fig. 2 (XI) is also to be recommended. In the top edge of the calorimeter two diametrically opposite notches are cut and a third horizontal copper rod of the shape shown is placed in the notches. Two copper plates are soldered to the rod and a small glass rod is fitted on to form a handle, which is given a to-and-fro motion. Inefficient stirring may cause an error of 10 or 20 per cent.

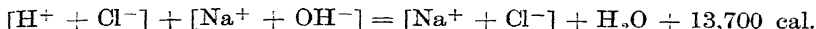
Mercurial thermometers are usually used; Mercury-in-glass thermometers rather than the enclosed 'Beckmann' type are now generally used for use in accurate calorimetry. They are, for example, adopted by the British Standards Institute. Resistance thermometers have advantages in certain work.

## CLASSIFICATION OF EXPERIMENTS

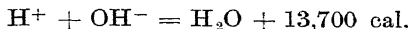
As examples of thermo-chemical methods we may take the determination of:

- (a) Heats of neutralization,
- (b) Heats of solution, dilution, and hydration,
- (c) Heats of formation.

**The Heat of Neutralization.** For dilute solutions of strong acids and bases this corresponds to the heat of formation of water from its ions, e.g.



i.e.



For concentrated solutions or for solutions involving weak electrolytes the amount of heat liberated will be changed by an amount equivalent to that required to complete ionization, &c.

**Determination of the Heat of Neutralization of Sodium Hydroxide by means of Hydrochloric Acid.**<sup>1</sup> As reaction vessel a cylindrical Dewar flask of 600 ml. capacity is convenient, and temperatures are to be read by means of Beckmann thermometers. The vacuum flask is fitted with a cork stopper bored with holes for the thermometer and the glass stirrer. The first step in the experiment consists in the determination of the water value of the calorimeter and its accessories. This is best done by following as closely as possible the procedure of the neutralization experiment, mixing equal quantities of water at different temperatures instead of the quantities of acid and alkali at nearly the same temperature.

Set the two Beckmann thermometers so that the mercury is near the bottom of the scale at room temperature. Mark one as 'alkali' thermometer and use this one always in the Dewar flask; the other may be referred to as the 'acid' thermometer. In the vacuum flask place 250 ml. of distilled water at a temperature about 4° above the room temperature and place the stopper with the thermometer and stirrer in position. Wash out another flask with distilled water and place 250 ml. of water at room temperature in the wet flask; fix the bulb of the 'acid' thermometer in the centre of the liquid and stand the flask in the outer jacket which is ordinarily used for a copper calorimeter. Gently stir both liquids and take the thermometer readings at intervals of 1 minute, taking, for example, readings of the temperature in the Dewar flask at the full minutes on the watch, and those of the temperature in the ordinary flask at the half-minute indications. Tap the thermometer before each reading is taken. After some preliminary irregularities the thermometers will begin to show a steady drift of temperature in one direction or the other. When both thermometers have shown this steady drift for 10 minutes, add the colder water to that in the Dewar flask, avoiding splashing; replace the cover, &c.; stir gently and take half-minute readings of the temperature of the mixture until a steady drift is again obtained for 10 minutes.

<sup>1</sup> From Rae and Reilly, *Physico-Chemical Practical Exercises* (Methuen), 1934.

The next step is to translate readings of the acid thermometer to those of the alkali thermometer.<sup>1</sup>

Tie both thermometers together so that the bulbs lie side by side and fix them in the Dewar flask in water about 4° above room temperature. Stir gently and after a few minutes tap and read the temperatures on both thermometers: repeat after 2 minutes and if the difference of readings remains unaltered we can use this as the factor for converting 'acid' readings to 'alkali' readings at this temperature. Repeat with water at 2° above and also at the room temperature. The three factors obtained may be used to plot a curve from which that at any scale reading can be obtained.

Convert the readings of the acid thermometer obtained in the first part of the experiment into alkali readings, so that now all temperatures are on this scale. Plot on squared paper the temperature readings of the two separate lots of water and of the mixture as ordinates and times as abscissae. Suppose that the last temperature reading before mixing was at the seveneenth minute and that the first temperature reading of the mixture was made at the eighteenth minute, we may take the time of mixing as 17½ minutes. Set up an ordinate to represent this time. With the temperature readings in each case we proceed until the temperature drift becomes steady for 10 minutes: extrapolate these straight lines until they cross the time of mixture ordinate and from these intersections read off  $t_1$ , the temperature of the hot water;  $t_2$ , that of the cold water; and  $t_3$ , that of the mixture. Let  $W$  be the water value of the calorimeter, together with the thermometer and stirrer. Then  $250 + W$  gram of water cooled from  $t_1$  to  $t_3$  and 250 gram of water warmed up from  $t_2$  to  $t_3$ :

$$\text{therefore} \quad (250 + W)(t_1 - t_3) = 250(t_3 - t_2)$$

$$\text{and} \quad W = \frac{250(2t_3 - t_2 - t_1)}{t_1 - t_3}$$

Prepare approximately N/4 solutions of the acid and base and determine their concentrations with accuracy by titration against a standard. It is convenient if the acid solution is slightly more concentrated than the alkali, so that on mixing equal volumes all the alkali will be neutralized. Having washed and dried all the apparatus, place 250 ml. of the alkali solution in the Dewar flask and place the stopper with the thermometer and stirrer in

<sup>1</sup> These temperatures will still not be in degrees Centigrade because the Beckmann degree necessarily varies with the amount of mercury in the bulb. These thermometers are generally set so that the degree corresponds to the Centigrade degree over the range 0° to 5°, for other ranges the values are

Temperature range	Degree value
- 35° to - 30°	0.982°
0° to 5°	1.000°
+ 20° to + 25°	1.009°
+ 30° to + 35°	1.013°
+ 45° to + 50°	1.020°
+ 95° to + 100°	1.037°
+ 145° to + 150°	1.050°
+ 195° to + 200°	1.058°
+ 245° to + 250°	1.060°

These corrections are not required in the present instance.

position. Wash out the wide-necked flask with the acid solution and to the wet flask add 250 ml. of acid ; place this in the outer vessel of the calorimeter and insert the 'acid' thermometer and stirrer. Read alkali and acid temperatures each minute, as was done in the water value experiment, and continue until the regular drift due to radiation has been steady for 10 minutes. Pour the acid into the alkali without splashing, noting the time of starting and finishing the pouring and taking the mean as the time of mixing. Read the temperatures of the mixture each half-minute until the steady drift has been maintained for 10 minutes. Convert 'acid' to 'alkali' temperatures.

The temperature of the acid ( $t_1$ ), the alkali ( $t_2$ ), and the mixture ( $t_3$ ) are then obtained by a graphic method, like that given for the water value. The heat change is then calculated as follows : a quantity of heat  $H$  given by the reaction has raised 250 ml. of sodium chloride solution from  $t_2$  to  $t_3$  and a further 250 ml. of sodium chloride from  $t_1$  to  $t_3$ , while the calorimeter (water value  $W$ ) has been raised from  $t_2$  to  $t_3$ . Then if  $d$  is the density and  $S$  the specific heat of the sodium chloride solution,

$$H = 250 \times S \times d(t_3 - t_2) + 250 \times S \times d(t_3 - t_1) + W(t_3 - t_2)$$

$S$  and  $d$  may be taken equal to 1 ; the error in each case is less than 1 per cent and they are of opposite sign, hence

$$H = 250(2t_3 - t_2 - t_1) + W(t_3 - t_2)$$

If the alkali was  $x$  . Normal and the acid slightly more than this,  $H$  is the heat change for  $x/4$  gram molecules of alkali, so that that for 1 gram molecule can be calculated.

**Correction for Radiation.** To obtain this latter, we may arrange that the acid and alkali are just so much below room temperature originally as the mixture is finally above it, so that the heat gained in the first half of the experiment balances approximately that lost in the second half. This method is difficult in practice and cannot be made very accurate. A graphical method which gives reasonable accuracy is represented in Fig. 3 (XI).

The parallel lower curves represent the temperatures of the acid and alkali before mixing. The upper sloping curve is that of the mixture cooling by radiation. Draw a vertical line through the time of mixing and produce

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16  
Time in mins

FIG. 3 (XI)

the curves to meet it at  $t_1$ ,  $t_2$ ,  $t_3$  ;  $t_1$  and  $t_2$  are then the temperatures of the acid and alkali at the time of mixing and  $t_3$  is the temperature of the mixed solution immediately on mixing.

The heat change is then calculated as follows : A quantity of heat  $H$  given out by the reaction has raised 250 ml. sodium chloride solution from  $t_2^\circ$  to  $t_3^\circ$ , and 250 ml. sodium chloride solution from  $t_1^\circ$  to  $t_3^\circ$ . If  $S$  is the



specific heat of the sodium chloride solution and  $W$  the water value of the calorimeter, stirrer, and thermometer, then if  $d$  = density of sodium chloride

$$H = S \times 250 \times d(t_3 - t_2) + S \times 250 \times d(t_3 - t_1) + W(t_3 - t_1)$$

The heat is then calculated for gram-molecular weights, knowing the strength of the solutions employed.

The water equivalent of the calorimeter is the correction for the heat given to this vessel during the rise in temperature. It is equal to (Wt. of cal. and stirrer)  $\times S_1$ , where  $S_1$  is the specific heat of the metal.

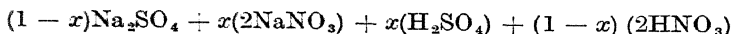
**Relative Strengths of Acids.** A somewhat similar process may be used to determine the relative strengths of acids. The principle used is the displacement of one acid from its salts by another acid according to the relative avidities of the acids. The heat change in the process is measured. The experimental procedure in determining the relative strengths of sulphuric and nitric acids is as follows:

*Experimental.* Molecular solutions of nitric acid, sulphuric acid, sodium sulphate and sodium nitrate are prepared. Determine the heat change  $H_1$ , when 500 ml. of nitric acid reacts with 250 ml. of sodium sulphate solution, and the heat change  $H_2$ , for the reaction of 250 ml. of sulphuric acid solution with 500 ml. of sodium nitrate solution. The heat changes are measured in the way already described. A larger Dewar flask is required, and its water value must be determined for a total water content of 750 ml.

In the experiments equivalent amounts of the various reactants have been used: let  $x$  be the fraction of the sulphuric acid displaced by the nitric acid from the sodium sulphate, then  $1 - x$  is the fraction not displaced, and  $x(1 - x)$  represents the relative strengths of the nitric and sulphuric acids;  $x(1 - x)$  also represents the ratio in which one equivalent of sodium hydroxide would be divided between one equivalent of nitric acid and one equivalent of sulphuric acid if these quantities were brought together.

In the second experiment, when sulphuric acid is added to sodium nitrate,  $1 - x$  is the fraction of nitric acid liberated and  $x$  is the fraction of sodium nitrate unchanged.

When one molecule of sodium sulphate reacts with two molecules of nitric acid in aqueous solution,  $2x$  molecules of sodium nitrate are formed and  $x$  molecules of sodium sulphate are decomposed so that the composition of the solution at the end of the reaction is



The net thermal effect will be the sum of the heat changes resulting from

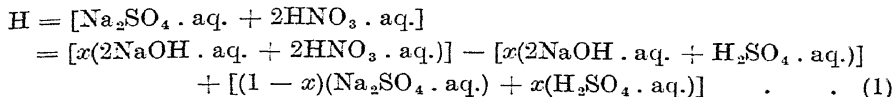
- (1) the decomposition of  $x$  molecules of  $\text{Na}_2\text{SO}_4$
- (2) the formation of  $x$  molecules of  $(2\text{NaNO}_3)$
- (3) the reaction of  $x$  molecules of  $\text{H}_2\text{SO}_4$  with  $(1 - x)$  molecules  $\text{Na}_2\text{SO}_4$
- (4) the reaction of  $(1 - x)$  molecules of  $(2\text{HNO}_3)$  with  $x$  molecules  $(2\text{NaNO}_3)$
- (5) the reaction of  $x$  molecules of  $\text{H}_2\text{SO}_4$  with  $(1 - x)$  molecules of  $(2\text{HNO}_3)$

Thomsen showed that (4) and (5) are negligible and that (3) could be expressed by the experimentally deduced formula

$$[\text{Na}_2\text{SO}_4 \cdot \text{aq.} + n \cdot \text{H}_2\text{SO}_4 \cdot \text{aq.}] = \frac{n \times 3,300}{n + 0.8} \text{ cal.} \quad (a)$$

According to Hess' Law if the three substances A, B, and C react in aqueous solution the total heat change will be the same whether they react simultaneously or in turn, provided that the initial and final states are the same.

The thermal reaction between two molecules of nitric acid and one molecule of sodium sulphate in aqueous solution may be expressed



The first two terms on the right-hand side of (1) represent the difference between the heats of formation of  $2x$  equivalents of sodium nitrate and sodium sulphate. This may be shown as follows.

If three substances A, B, and C (e.g.  $2\text{HNO}_3 \cdot \text{aq.}$ ,  $2\text{NaOH} \cdot \text{aq.}$ , and  $\text{H}_2\text{SO}_4 \cdot \text{aq.}$ ) react in aqueous solution, the results are the same, provided that the initial and final states are the same, whether the substances react simultaneously or in turn (Hess' Law).

This may be expressed

$$[A + B + C] = [A + B] + [AB + C] = [B + C] + [BC + A]$$

$$\text{therefore} \quad [B + A] - [B + C] = [BC + A] - [AB + C]$$

If  $A = 2\text{HNO}_3 \cdot \text{aq.}$ ;  $B = 2\text{NaOH} \cdot \text{aq.}$ ; and  $C = \text{H}_2\text{SO}_4 \cdot \text{aq.}$ ,

$$\begin{aligned} &[2\text{NaOH} \cdot \text{aq.} + 2\text{HNO}_3 \cdot \text{aq.}] - [2\text{NaOH} \cdot \text{aq.} + \text{H}_2\text{SO}_4 \cdot \text{aq.}] \\ &= [\text{Na}_2\text{SO}_4 \cdot \text{aq.} + 2\text{HNO}_3 \cdot \text{aq.}] - [2\text{NaNO}_3 \cdot \text{aq.} + \text{H}_2\text{SO}_4 \cdot \text{aq.}] \end{aligned}$$

Then if  $H_1$  and  $H_2$  have the significance given above

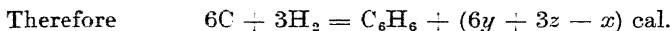
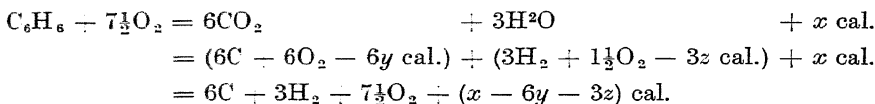
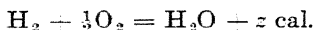
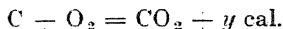
$$\begin{aligned} H &= 4H_1 \\ &= 4x(H_1 - H_2) + \{(1-x)(\text{Na}_2\text{SO}_4 \cdot \text{aq.}) + x(\text{H}_2\text{SO}_4 \cdot \text{aq.})\} \\ &\quad \text{from (1);} \\ &= 4x(H_1 - H_2) + (1-x)\left\{(\text{Na}_2\text{SO}_4 \cdot \text{aq.}) + \frac{x}{1-x}(\text{H}_2\text{SO}_4 \cdot \text{aq.})\right. \\ &\quad \left. \times \frac{3,300}{1-x} - (1-x)\right\} \quad \text{from (a)} \\ &= 4x(H_1 - H_2) + \frac{x(1-x) \cdot 3,300}{0.2x + 0.8} \end{aligned}$$

Hence from  $H_1$  and  $H_2$  we can calculate  $x$  and from this  $x/(1-x)$ .

(b) **Heat of Solution, &c.** When a gram molecule of salt is dissolved in a large amount of solution which is already practically saturated we obtain *The Last Heat of Solution*, which is the important quantity in connexion with the temperature and pressure coefficients of solubility. On dilution of a saturated solution a further heat change occurs, owing to ionization, &c., so that *Heats of Dilution* can be measured. The heat of dilution from concentration  $c_1$  to concentration  $c_2$  is the heat change when that volume which contains 1 gram molecule at the concentration  $c_1$  is diluted until the concentration is  $c_2$ . Hence, if a gram molecule of the salt is dissolved in variable amounts of water, variable amounts of heat will be set free or absorbed

according to the final dilution. Three cases are distinguished and are indicated by the terms (1) *First Heat of Solution* when 1 gram molecule is dissolved in a very large amount of water so as to give an ideal solution, (2) *Total Heat of Solution* when only sufficient solvent is used to give a saturated solution with the 1 gram molecule of solute, and (3) *The Last Heat of Solution* when the solute is dissolved in a very large amount of solution which is already practically saturated.

*The Heat of Hydration of a Hydrate* is the thermal change which occurs when a gram molecule of the anhydrous salt combines with sufficient water to form the crystalline hydrate. It can readily be measured by determining the difference between the heats of solution of (1) the anhydrous salt and (2) the hydrated salt, in corresponding quantities of water, i.e. allowing for the water combined as water of crystallization. *The Heat of Formation* is the thermal change when 1 gram molecule of a compound is formed from its elements: it is rarely possible to determine this directly so that it is generally obtained by the application of Hess' Law: thus the heat of formation of benzene may be obtained from a knowledge of its heat of combustion together with the heats of formation of carbon dioxide and water: e.g.



**Determination of the Heat of Solution of Copper Sulphate and its Heat of Hydration.** The heat of solution to be determined in this experiment is not one of those defined above, but is the heat change observed when 1 gram molecule of copper sulphate is dissolved to form an N/10 solution, i.e. 160 grams are dissolved in 10 litres of water. In the experiment 6.4 grams of the anhydrous salt in 400 ml. of water will give a rise of about  $1.5^\circ$ , so that this is a convenient quantity to use and from the result by multiplying by 25, the molecular heat of solution can be calculated.

For this experiment the simple form of calorimeter described by Nernst may be used. This consists of a 600 ml. glass tall-form beaker which is placed inside another of the same form and of 800 ml. capacity, and insulated from it by strips of cork. Temperatures may be measured with an ordinary thermometer graduated in  $0.02^\circ$ . A wooden cover is provided, pierced with holes to take the thermometer, a glass stirrer and a test tube. The water value of the calorimeter may be calculated in this instance from the weight of the beaker, stirring rod, thermometer (the thermal capacities of equal volumes of mercury and glass are approximately the same), &c., and the specific heat of glass (0.19); allowance may be made for that part of the apparatus which is above the water level and, owing to the low conductivity of glass, will not be heated appreciably. In the case of the thermometer, for example, it may be immersed in water in a narrow measuring cylinder up to the height it will be immersed in the calorimeter and the displacement

read off. This method of determining the water value is not so accurate as the direct method, but will be sufficiently near for our purpose.

Dry two test tubes of thin glass in the oven and fit them with corks. Weigh out two 10-gram portions of powdered copper sulphate crystals and place one portion in one of the dried test tubes and stopper it. Heat the other portion in a crucible over the Bunsen flame until all the water of crystallization is driven off and the salt is quite white; then transfer it, while still hot, to the second test tube and stopper it at once. In the beaker place 396.4 ml. of distilled water, fix the thermometer so that its bulb is in the centre of the liquid, and put the stirrer and cover in place. Smear the outside of the test tube containing the hydrated crystals with a very little vaseline to prevent the adherence of water as much as possible and then fix this so that the surface of the powder is below the water level in the calorimeter. Wait 10 minutes for temperature equilibrium to be set up and then start to read the temperature at half-minute intervals, stirring regularly all the time and tapping the thermometer lightly before each reading. When a steady drift has been established for 10 minutes, add the contents of the test tube to the water as quickly as possible, put the cork in the hole from which the test tube was removed, continue the regular stirring and resume the temperature readings at the next whole minute, and continue until a regular drift is once more maintained for 10 minutes. Treat the temperature readings as described, and from the graph obtain the rise of temperature  $t$ . If  $h_1$  is the heat evolution and  $W$  the water value of the calorimeter

$$h_1 = (W + 396.4) \cdot t$$

Repeat the experiment, using the anhydrous salt and 400 ml. of water, and so obtain the heat evolution  $h_2$ .

The heat of hydration is then  $25(h_2 - h_1)$  and the heat of solution  $25h_2$ .

**Adiabatic Calorimeter.** Practically all thermal measurements that are carried out with the type of calorimeter described can be placed under one or other of the above headings. The important source of error in the apparatus has been seen to be the faulty heat insulation of the innermost vessel. To eliminate this error Richards has devised various forms of calorimeter in which the bath surrounding the calorimeter is kept at an equal or equivalent temperature throughout the experiment. The device has been found to be particularly convenient in work on heats of dilution and heats of reaction. Richards has employed chemical reaction in the outer vessel to raise the temperature at the same rate as the inner, but in general, electrical heating is found more satisfactory. MacInnes and Braham have used the same type of calorimeter in their researches on heats of dilution. Richards' method is modified so that the environment is kept about  $0.15^\circ$  lower than the calorimeter during the experiment. This corrects effects of stirring, radiation, evaporation, &c. A diagram of their apparatus is given. The following is the author's own description of the instrument:

'The calorimeter vessel A-A (Fig. 4 (XI)) is 21 cm. deep and is separated on the sides and bottom by a 6 mm. air space from the vessel B-B. Both of these vessels are made from heavy copper and nickel-plated. Separation of the two vessels is provided by the gasket  $a$ , made of rubber tubing, and by the supporting ring of hard rubber. The seams of both these vessels are

brazed, not soldered. Vessel B-B is supported on three brass legs that fit into holes in a wooden false bottom in the larger vessel C. The vessel B-B carries the cover M-M of 3 mm. brass, which can be clamped into the 2 cm. flange of the vessel B-B. A rubber gasket *e-e* is interposed between the

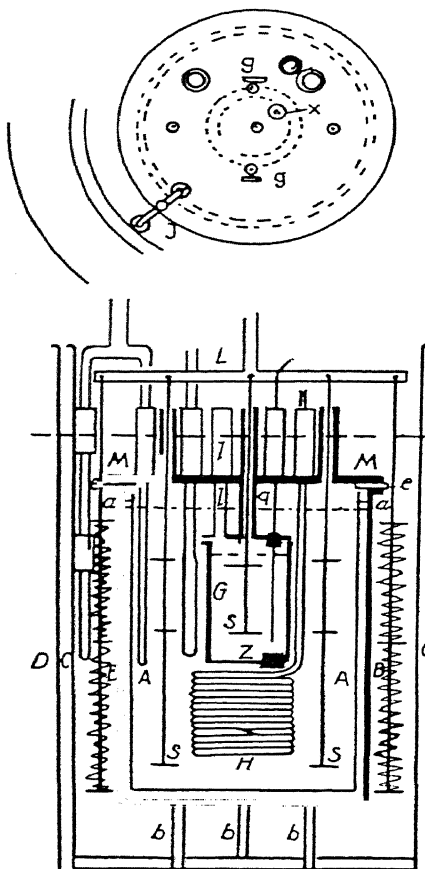


FIG. 4 (XI)

covers and the flange. Screwed into the cover are a number of tubes each 2 inches long, through which pass a platinum resistance thermometer, the leads from the heater H, the arms from the stirrers S, S, S, the wire supports *g-g* of the dilution cup G, one leg of the thermo-junction J and the rod X. The tube *l* is for filling the dilution cup.

**The Dilution Cup.** The sides of the dilution cup G are made of thin

sheet copper, fastened to a brass ring at the top and to a sheet brass bottom. A brass cover 3 mm. thick carries the tubes  $l$  and  $q$ . This cover makes a water-tight connection with the ring at the top of the cap, by means of the rubber gasket and screws as shown. The tube  $l$  fits under the second tube  $l$  and is used for filling the cup. The middle stirrer  $S$  passes through the tube  $q$ . The cup is held in place by means of wires fastened into tubes in the cover M-M.

‘**The Stirrer.** The stirrer S-S consists of four brass discs, 18 cm. outside and 12.7 cm. inside diameter, each with ten 16 mm. holes punched at intervals. Water is poured between the vessels B and C, and to a depth of 3.8 cm. over the cover M-M. The space occupied by this water will be referred to for convenience as the “surroundings”. In this space fits the annular stirrer shown between B and C in diagram, consisting of three galvanized iron discs of 24 cm. internal and 32 cm. external diameter, each disc containing eight holes. The stirrer carries four coils, each containing 8 metres of No. 18 nichrome wire. The coils pass through the stirrer discs on wooden insulators and are arranged diagonally to the direction of motion of the stirrer. These coils are connected in series through a key to a source of 110-volt alternating current. By means of this arrangement the temperature of the surroundings can be arranged at any time.

‘The stirrers S, S, S and the outside stirrers are all connected to the yoke L, which is given an up-and-down motion of 5 cm. sixty times per minute by means of a crank, operated through a system of pulleys, by a  $\frac{1}{8}$  h.p. electric motor. Experiments have shown that with this system of motion stirring is very efficient. Introduction of heat through the heating coils is immediately responded to by the thermo-junction system.

‘**Jackets.** The vessels, C, D-P, and E are of heavily galvanized iron. D-P is separated from C by an air-space. The space between the vessels D-P, and E was originally designed to give a very rough regulation of the radiation from the “surroundings”. It was found, however, that closer regulation of the temperature of the water in this space made the regulation of the “surroundings” very much easier. Accordingly a stirrer was constructed of light metal rods. The stirrer carries heating coils similar to those on the stirrer in the “surroundings”. It is connected to the yoke which operates the other stirrers, but is not shown in the drawing.’

The above detailed description is given as an example of the painstaking care necessary to obtain accurate, reliable results in thermo-chemical work. Very accurate reading platinum-resistance thermometers were used in the experiments.

An accuracy of about 0.1 per cent. was obtained by these experimenters.

**Heat of Combustion** is the heat developed in the complete combustion in oxygen of 1 gram molecule of the substance. The determination is largely confined to organic substances where the products are mostly confined to carbon dioxide and water: the determination is an important one because, with a knowledge of the heats of formation of carbon dioxide and water and the heat of combustion of the compound, we can calculate the heat of formation of the compound by subtracting the latter from the sum of the two former. Heats of combustion are also of practical importance in the case of fuels; here they are usually recorded as heats of combustion of 1 gram of the

fuel if it is liquid or solid or per cubic metre if it is gaseous ; the results are here known as the ' calorific values '. The heats of combustion of liquids and gases may be determined with the aid of Thomsen's universal burner and calorimeter.

**Thomsen's Method.** The pioneers in measurements of heats of combustion, as in thermo-chemistry in general, were Berthelot and Thomsen. Thomsen has based his researches upon an examination of volatile organic substances and has measured the heat of combustion in the state of gas or vapour. The method is reduced to its simplest form when dealing with gases. In this case the dry gas is collected over mercury in a gasometer, and then led with a regulated velocity into the calorimeter, where it is burnt in oxygen. Where the gas has a high percentage of carbon, it is diluted in the gasometer with nitrogen or air in such a manner that the oxygen in the mixed gases amounts to from 40 to 50 per cent by volume. When the substance under examination is not a gas a ' *universal burner* ' is used, in which it is burnt in the state of vapour. The burner is illustrated in Fig. 5 (XI). The liquid to be burnt is placed in the small bulb *a*, and passes up by means of purified cotton or asbestos into the tube *b* where it is heated. The tube *b* is surrounded by a larger glass tube *d*, and between these two tubes there is a spiral of fine platinum wire, the extremities of which are represented in the diagram by the letters *e* and *p*.

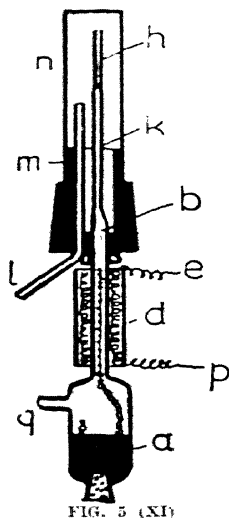


FIG. 5 (XI)

By passing an electric current through the spiral the wick can be raised to any desired temperature. The tube *d* is enveloped in paper to prevent too rapid cooling. When the temperature of ebullition has been reached vaporization takes place with a velocity dependent upon the intensity of the current. As long as a regular current is maintained the evolution of vapour remains constant and the size of the flame does not vary at *h*. In order to prevent any condensation of the vapour in its passage from *b* to *h* a double wire of silver is introduced into the tube *h*. This tube, which is formed of a piece of platinum foil, becomes strongly heated and communicates heat

to the silver wire from *h* to *b*. This prevents the vapour from becoming cooled and at the same time does not produce any modification in the quantity of heat supplied to the calorimeter.

If a current of gas is to be used to volatilize the substance, either for the purpose of forming a vapour of suitable density for the combustion, or else to effect its combustion by mixing with hydrogen, the gas is introduced through the opening *q* of the lower bulb. The rate of flow of the gas and the intensity of the electric current must then be regulated to give a flame of the requisite size, without smoke or deposition of graphite.

The universal burner is connected to the calorimeter (see below) in the following manner. In the india-rubber cork, which closes the aperture of the calorimeter, there is a short glass tube *k*, the internal diameter of which

is about 3 mm. larger than that of the tube *b*. Between these two tubes there is a ring of india-rubber which joins them firmly together. The air space between these two tubes, *k* and *b*, which is filled with glass wool, helps to insulate the heat of the tube *b*. The end of the combustion tube *h* is made of platinum foil, soldered into the tube *b*.

The tube *l* through which the oxygen passes is inserted through the rubber cork, outside the tube *k*. The upper part of this tube is surrounded by a larger tube, closed at the top in order to distribute the current of oxygen more uniformly.

Next to the india-rubber stopper is a disc of cork *m*, of somewhat smaller diameter, which serves to support a tube *n*, made of platinum foil. This platinum tube surrounds the two tubes through which enter the oxygen and the vapour to be burnt; its object is to render the oxidation more effectual, and for this purpose it is filled with glass wool up to the lower part of *h*. The current of oxygen is regulated in such a manner that the products of combustion on issuing are mixed with about 50 per cent of free oxygen.

**The Calorimeter.** The calorimeter used by Thomsen is represented in Fig. 6 (XI). The interior is of platinum and consists of a combustion chamber *a*, of 200 ml. capacity, surrounded by a spiral tube *c-c*, 1.8 metres long and 5 mm. in diameter, through which the gases pass to the absorption tubes. At the bottom of the combustion chamber is an opening into which a conical platinum tube is soldered. This tube serves to support the combustion chamber within the outer chamber of the calorimeter, through the floor of which it is soldered. The universal burner is inserted into an opening and is connected up with the tubes conveying the oxygen and the substance about to undergo combustion.

The calorimeter chamber *A*, which has a capacity of about 3 litres, is made of brass and is supported on three points fixed to a tripod stand; it is closed at the top by means of an ebonite cover *e*. It was not necessary to surround the calorimeter with a number of jackets since it was possible to arrange that the temperature of the laboratory, where the experiments were carried out, did not vary more than one-tenth of one degree during the course of several hours. The calorimeter thus stands free in the air, and is simply protected by an ebonite cylinder *d*, open at each end, from any possible radiation from the person of the experimenter. This screen is supported upon three points, and in no way interferes with the free circulation of the air round the calorimeter.

The water in the calorimeter is kept in continual circulation by means of a circular stirrer passing between the walls of the combustion chamber and the spiral tube; the stirrer is worked by a small motor.

There are four openings (not shown) in the ebonite cover of the calorimeter, one for the thermometer, another for the spiral tube, while the other

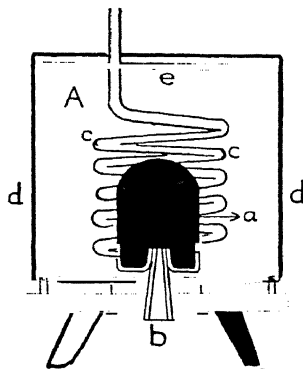


FIG. 6 (XI)



two serve for the passage of the wires in connection with the stirring apparatus.

**General Method.** The quantity of water in the calorimeter is weighed. The gas or vapour to be burnt and the oxygen for the combustion are aspirated through the system via the *universal burner*. The gaseous products of the combustion issue through an opening of the platinum spiral and are absorbed in a battery of chemically-prepared U-tubes. These are weighed before and after the combustion.

The temperature of the calorimeter is read for a few minutes before the combustion. The latter is continued till the temperature has risen as high as is required. The burner is then disconnected from the calorimeter and dry air aspirated through the apparatus. The temperature is read every 3 minutes for a quarter of an hour. The experiment is then complete.

## SECTION 2: BOMB CALORIMETER

The more usual method for determining the heats of combustion, both in scientific and commercial practice, is the use of the instrument known as the bomb calorimeter. This method was first used by Berthelot, and consists essentially in burning the substance in excess of oxygen at high pressure in a bomb immersed in water; the heat of combustion is then determined by the rise in temperature of the water. Having the necessary apparatus the method is much simpler to use than that of Thomsen. The duration of the experiment is short, combustion being practically instantaneous. The method may be used for non-volatile substances, and for solids as well as liquids.

**Calorimeter Apparatus.** The calorimeter outfit consists of the following elements:

- (1) The bomb
- (2) The calorimeter vessel and stirrer
- (3) The heat-insulating jacket.
- (4) Accessory apparatus, including a clamp and spanner for closing the bomb, appliances for filling the bomb with oxygen (cylinder, manometer, &c.), a mould and press for moulding powdered substances into pellets, electrical ignition apparatus and stirring machinery.

**The Bomb.** The bomb is a modification of that of Berthelot: the great objection to the latter is its cost, owing to the amount of platinum in the cover and lining. Various modifications of the Berthelot apparatus have been devised to obviate the expense of the platinum. Mahler uses a bomb of forged steel with enamel lining. Hempel uses a steel bomb without lining. In one of the oldest forms—the Mahler-Donkin—the bomb consists of a massive gun-metal cylinder provided with a cover held down by three studs. The bomb is plated with gold internally to resist the corrosive action of acids developed during the combustion. In the more recent bomb developments thin platinum is used internally; Atwater and Snell have designed a type of bomb which is found satisfactory. The following is a description of the Atwater and Snell bomb.

The bomb consists of three parts: a cylindrical cup to contain the substance to be burnt and the oxygen for combustion, a cover to close the cup and a threaded ring or *collar* to hold the cover tightly on the cylinder. With these is a metal capsule to hold the substance.

The cap is of Hotchkiss gun steel. The cover, collar C, and screws EF (Fig. 7 (XI)) are of best tool steel. The inside dimensions of the cup are: depth 12.7 cm., diameter 6.3 cm. at top, and 5.9 cm. at bottom. The wall is approximately 0.6 cm. thick. The capacity of the bomb is 380 ml.

The cover is lined on the bottom with platinum and is provided with a neck D. Into this fits at the top a cylindrical screw E, into which in turn

fits a valve screw F. In the neck D, where the bottom of the screw E rests, is a packing of lead. The pressure of the valve screw on this packing makes a tight closure on the part of F which it surrounds. On the side of D is an opening G, into which may be screwed the coupling connecting with the oxygen cylinder. The coupling when screwed in thrusts against a washer at the end of G, which ensures perfect closure.

The platinum wires inside the bomb serve to hold the capsule O containing the substance and to conduct the electric current for starting combustion.

The lining of both cup and cover is platinum; the best substitute for the metal was one of copper heavily electroplated with gold. The metal of the capsule is platinum, sometimes nickel.

The *Krocker* type of bomb (see below) has a cover screwed on to the bomb. The bomb is of steel while the cover is of bronze. It has a fixed platinum lining. Parr<sup>1</sup> gives the results of investigations to provide a base metal alloy which is suitable for bomb-casting and non-corrosive by acids. His researches show very promising results. The composition of the alloy found most suitable is as follows (carbon, boron or titanium not determined):

Cu	6.42
Mn	0.98
Si	1.04
W	2.13
Ni	60.65
Al	1.09
Fe	0.76
Cr	21.07
Mo	4.67
	<hr/>
	98.81

A bomb of this material need not then be platinum-lined.

The Mahler-Cook bomb calorimeter (made by C. W. Cook & Sons, Leicestershire) is very suitable for general calorimetric determinations of coal, oil, &c., and is accurate and easy to manipulate. The bomb or pressure vessel, in which the material under investigation is burnt in compressed oxygen gas, is shown in vertical section in the figure (similar to Fig. 7 (XI)). It is 650 ml. capacity, and is made of mild forged steel. The inner surface is coated with a special enamel to protect the steel against corrosion.

The cover, which carries the valve for the introduction of the oxygen, is provided with insulated firing plug, and platinum or nickel supports for the crucible and ignition wire. This cover is connected to the main vessel by a hexagon nut and special spigot joint, which allows the nut to be screwed up without turning the cover, and avoids tearing the lead joint.

A double-walled copper vessel insulated on the outside with a thick layer of felt forms the enclosure for the calorimeter. It is surmounted by a framework holding a universal pulley for the stirring gear, and is provided with an aluminium cover and mounted on a cast-iron base.

The bomb when prepared and charged with gas is placed in an inner copper vessel containing 2,500 ml. of water. This copper vessel is nickel-plated, and insulated at the bottom from the surrounding vessel by cork studs.

<sup>1</sup> *J. Amer. Chem. Soc.*, 1915, 37, 2515.

The stirring gear is actuated by hand from any required distance by a cord passing over the pulley mentioned above. If the cord be attached to the large pulley it may be operated by means of a small motor.

A small screw coal press is used for making the cylinders of compressed coal or other material, the calorific value of which has to be determined.

A split die receives the powdered material, which is filled in and pressed down with the steel rod by hand and subsequently strongly compressed by means of the screw. In order to remove the briquette thus formed, the die is opened.

A thermometer divided into 100ths of a degree Centigrade and with a

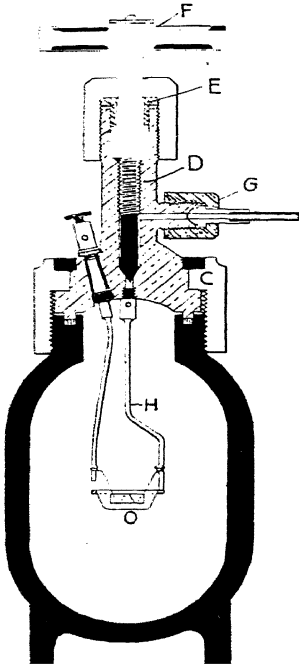


FIG. 7 (XI)

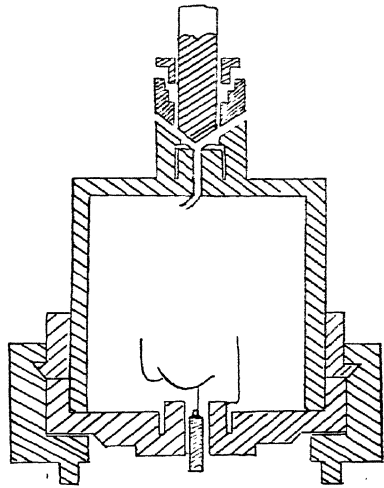


FIG. 8 (XI)

range of about  $8^{\circ}$  is used, or alternatively a Beckmann type with adjustable zero, and also a thermometer divided into tenths of a degree for the preliminary adjustment of the thermometer and for taking the temperature of the outer vessel.

A tapping key or switch is employed, together with flexible wire connexions, for making contact when firing the charge in the bomb. With the Mahler-Cook bomb it is recommended to use a battery for ignition, but as an alternative a rheostat for working off the electric supply mains may be employed.

The staff of the U.S. Bureau of Mines has developed a form of bomb suitable for accurate work. Fig. 8 (XI) shows the bomb, consisting of a

gold-plated monel metal shell of about 600 ml. capacity. This metal is preferable to steel in that it is gold-plated more easily. This latter process is very difficult, but if properly performed the surface is practically indestructible. The cover-locking arrangement—an adaptation of the principle used in breech pieces of cannon—consists of a tough steel receiving nut and lock, so contrived that less than one-eighth of a revolution suffices for sealing. A circular gasket of electrician's solder completes the seal. This design possesses the advantage that if the lock wears out in service a new one can be fitted to the gold-plated bomb.

Robertson and Garner have described a bomb suitable for the calorimetry of high explosives. The bomb is of vanadium steel, cylindrical in shape, about 12 inches long and 3.9 inches in external diameter. The walls and bottom of the bomb are lined with steel and the bottom protected by a steel disc, replaced after each measurement. The actual firing chamber is 6 inches long and 1.76 inches internal diameter. The free space in the bomb is approximately 235–240 ml.

**Griffin-Sutton Combustion Bomb for Fuels.**<sup>1</sup> The design of some of the older forms of bomb calorimeters is conspicuously good in view of the materials available at the time. Fundamental alterations, however, are now desirable so as to make use both of stainless steel and of rubber. This

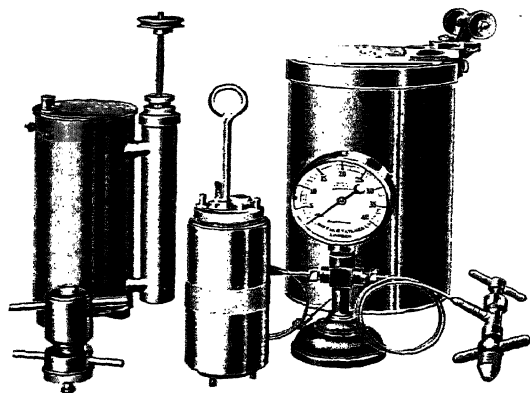


FIG. 9 (XI)

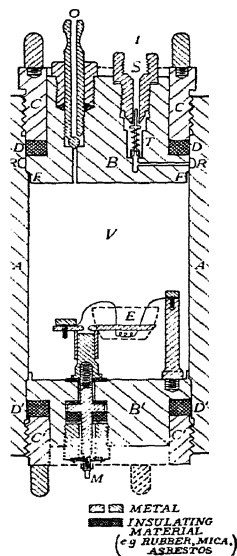


FIG. 10 (XI)

apparatus, in its commercial form, attains an accuracy of 0.1 per cent on the calorific value; the calorimeter and some of the auxiliary equipment is shown in Fig. 9 (XI). The fuel lies in E (Fig. 10 (XI)), and is surrounded by an atmosphere of compressed oxygen in the vessel V. The vessel is

<sup>1</sup> Made by Griffin and Tatlock, London. Sutton, *J. Sci. Inst.*, 1933, 10, 286.

placed in water in a calorimeter, and the fuel ignited by means of an electrically heated wire.

The seal is secured by means of gentle hand-pressure. It can be applied equally well to the top and to the bottom of the vessel; the pot-shaped vessels of earlier designs are therefore replaced by the cylindrical tube A. The head and base, B and B', close the tube A as indicated in the diagram, and are held in position by the locking collars C and C'. These latter are screwed in loosely by hand, so as just to make contact with the annular washers D and D'. Subsequently, when V is filled with the high-pressure oxygen necessary for the combustion, B and B' move outwards compressing D and D' so as to form gas-tight joints. On releasing the pressure, when the measurements are finished, B and B' immediately move inwards again releasing the pressure on D and D' so that C and C' can be removed by hand. With this design, therefore, no spanner is required.

Separate inlet and outlet valves, I and O, have been provided. The oxygen cylinder is connected to the socket S. The incoming gas passes through a non-return valve T such as is used in the tyre of a motor-car, and issues into the annular chamber RR, from which it finds its way into the main chamber V. The flange FF is sufficiently long to deflect the incoming gas so as to form a cylindrical stream down the sides of the vessel. On meeting the base, the stream is deflected inwards and upwards and mixes turbulently in the space below the crucible E. When the gas is introduced in this way, the region of turbulent mixing does not extend above the capsule and the charge, even if powdered, remains undisturbed.

The water equivalent is as low as 1,800 grams. This corresponds with a temperature rise of approximately 5° per gram of naphthalene, 4.5° per gram of anthracite, 2.5° per gram of 'brown' coal, and 4° per millilitre of petrol. If an accuracy of 0.3 per cent is sufficient, the outer thermal shield may be a copper cylinder; for greater accuracy, a water jacket is necessary. The efficiency of the stirring is improved if the combustion vessel is not placed centrally in the calorimeter. Any form of asymmetry favours mixing. It is convenient that the electrical connexions should be made automatically on placing the combustion vessel in the calorimeter.

**The Calorimeter Vessel, Stirrer and Jackets.** The calorimeter cylinder is made of various metals or alloys. Atwater and Snell use one of Britannia metal 13 cm. diameter, 23 cm. high, and holding, with the bomb, nearly 2 litres of water. A stirrer moved by a small motor keeps the water in motion. It consists of two perforated annular pieces of sheet brass connected by two brass rods which project out of the calorimeter and are there attached by thumb-screws to a nickel-plated cross-piece. A groove is cut in one side of the annular brass-pieces to admit the thermometer. The calorimeter cylinder stands on cork supports to insulate it from the surrounding vessels.

The outer constant-temperature jackets, of indurated fibre, are such as to leave an air space of about 1 cm. between the two pails and one of 3 cm. between the inner pail and the calorimeter cylinder. The covers of the pails are of hard rubber. They are provided with holes for the two rods of the stirrer and for the thermometer. The arrangement of the bomb, calorimeter vessel and jackets is shown in section in Fig. 11 (XI).

The staff of the U.S. Bureau of Mines have also described an apparatus especially suitable for routine combustion calorimetry. The calorimeter is made of heavy sheet brass reinforced at the top and middle by brass bands. A tubular stirrer-holder is soldered to the calorimeter as shown in B (Fig. 12 (XI)). An electrode is fixed to the bottom of the calorimeter, but insulated from it, which makes contact with the bomb plug when this is placed in position.

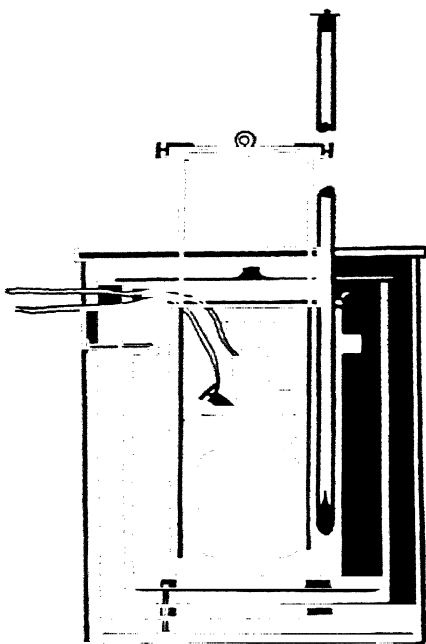


FIG. 11 (XI)

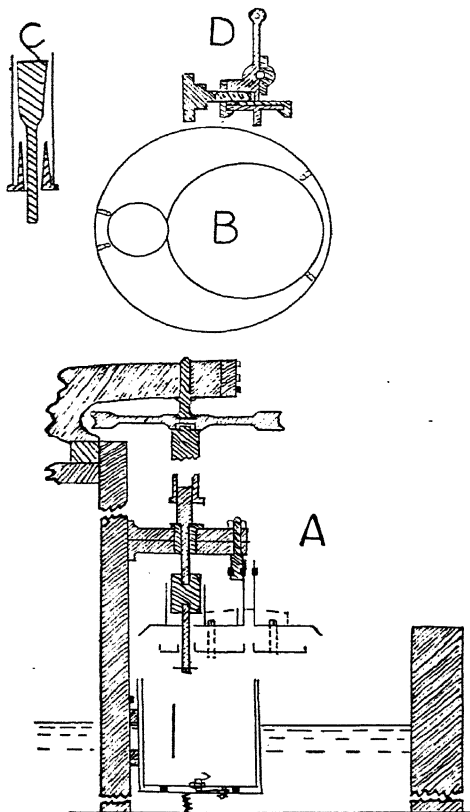


FIG. 12 (XI)

The calorimeter is supported in its jacket on three ivory studs. The jacket is a cylindrical vessel provided with a brass cover ground to a water-tight fit. Soldered to the jacket are two heavy brass lugs by which it is held to the vertical brass T-bar of the frame, in such a manner as to permit the jacket to slide vertically. The jacket is supported by a heavy brass spring fixed to the bottom of the tank, and of such strength that the jacket when charged is held vertical with its top slightly above the surface of the tank water against an adjustable stop fixed to the T-bar (A).

The stirrer shaft arrangement is also shown in the figure. The upper part of the shaft, on which the driving wheel is mounted, consists of a thick-walled brass tube, into which the lower part of the shaft telescopes, the latter being provided with a conical piece (C) screwed to the end, which engages a receiver at the lower end of the shaft tube after the manner of a conical friction clutch, when the whole calorimeter is lowered into place. The lower bearing of the stirrer shaft is carried by the lid bracket (D), which is held to the vertical T-bar of the frame by a clamp which permits of raising

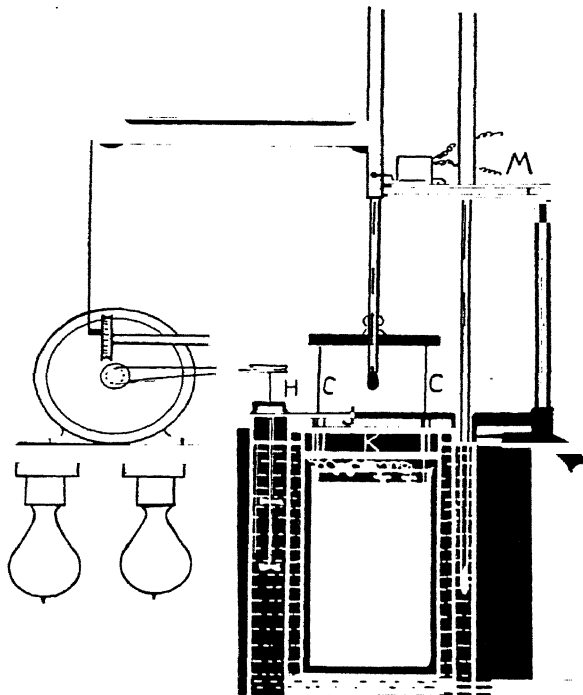


FIG. 13 (XI)

and lowering the lid and clamping in any desired position. The jacket can and cover are totally immersed in the water of the tank during an observation, and the position of the propeller stirrer is such that when the calorimeter is charged and the lid closed, the stirrer propeller has always the same position in the stirrer well. Electrical arrangements are provided to adjust the temperature in the calorimeter can to within  $0.01^{\circ}$  of that desired.

Benedict and Higgins<sup>1</sup> have described a calorimeter for use with the bomb in which the surroundings vary in temperature with that of the calorimeter vessel. The method is an adaptation of that of Richards and of

<sup>1</sup> *J. Amer. Chem. Soc.*, 1910, 32, 461.



MacInnes and Braham previously described. A diagram of their complete apparatus is given (Fig. 13 (XI)). The previous description of the method practically applies.

**Measurement of Temperature.** Usually mercury thermometers of the Beckmann type are employed. Sticking of the mercury in the bore is overcome by an electric buzzer tapping arrangement. For high-precision work resistance thermometers must be used; thermo-junctions have also been employed.

**Preparation of Sample.** For solid substances it is usual to compress the solid into a pellet or tabloid. This is done by first powdering the substance and then compressing it in a pellet press. Liquids are usually absorbed in blocks of pure cellulose; a blank test with the cellulose alone is first necessary.

**Quantity of Substance.** The weight of substance used varies with its composition; it is usually calculated to give a rise of about  $2^{\circ}$  in the bomb. The weight varies between 0.5 and 1.5 gram.

**Oxygen Pressure.** The quantity of oxygen required is about three times that which will unite with the charge to give complete combustion. The pressures used vary from 20–27 atm., or 300 to 400 lb. per square inch.

**Fusion Apparatus.** The ignition of the sample in the bomb is brought about by a small coil of iron wire heated by an electric current. A spool of wire is usually supplied with the apparatus. About 2.5 inches of wire are required for each combustion. The weight of the wire must be known. Ten or 12 volts from accumulators may be used or 110 volts connected through a bank of lamps.

**Determination of the Water Equivalent.** The heat capacity of the bomb and fittings must be known before conducting experiments. Two standard methods of effecting this calibration are employed: (1) by an electrical method based on putting into the system a known amount of heat measured as electrical energy; (2) by burning substances whose heating value is already known.

The electrical method may be made very accurate, but the apparatus is elaborate and time-consuming. Further, the conditions are not the same as during a combustion. The second method is much more common. It involves no extra apparatus and reproduces the exact conditions of the final experiment. The standard substances generally used are naphthalene (9,668), benzoic acid (6,324), or cane-sugar (3,988). The values indicated are the thermo-chemical values in calories corresponding to 1 gram of the different substances.

**Method of Working.** Powder and press into tablets a substance of known heat of combustion, e.g. naphthalene or pure salicylic acid. Weigh out about 0.7 gram of the substance in the case of the former. Place it in the metallic capsule provided. The best method of ignition is with cotton thread; when iron wire is used globules of melted iron fall on the bomb lining and may damage it. A piece of very fine platinum wire is stretched between the terminals; a known weight or known length (the weight of a given length having been previously determined) of dry cotton thread is tied to the middle of the thin platinum wire and the ends of the thread made to touch the weighed substance in the crucible. When the current is passed momentarily

the platinum wire glows or fuses locally and ignites the thread, which in turn ignites the substance. The allowance made for the thread (cellulose) is 3.852 calories per gram. If iron wire is preferred cut off 5 cm. of the iron wire provided, weigh it, and connect it to the electrodes (H) so that it passes round the capsule. Place the bomb in the stand and, by means of the large spanner, close down the cap. Connect the oxygen cylinder to the pressure gauge and so to the tube at G, and allow the bomb to fill until the pressure is 20–27 atm. Close the valve and remove the cylinder. Arrange the temperature of the calorimeter so that the water is about 2° below atmospheric temperature. At the close of the combustion the calorimeter will approximate to atmospheric temperature; this minimizes radiation losses. The weight of the water in the calorimeter must first be obtained. The bomb is then lowered into the calorimeter and the latter fixed in its surroundings. The covers are put on, the thermometer fixed and the stirrers set in motion. As soon as the different parts of the calorimeter have assumed a common temperature, the mercury will begin to rise at a uniform rate and the pre-combustion readings must be taken. The temperature is read every minute for 7 to 10 minutes. The electrical connexions being made, the circuit is closed for a moment at a definite time. Readings are again taken every minute throughout the rise of temperature and the highest temperature noted; the readings are continued for 10 minutes during cooling.

The bomb is then removed from the calorimeter, blown off and opened; any unburnt iron is removed and weighed. The oxides of nitrogen produced may be determined and corrected for in the heat calculation.

The temperature correction may then be obtained by the method already described or by using the equation

$$T = T_m + n\theta + \frac{\theta' + \theta}{2}$$

where  $T$  = corrected temperature rise

$T_m$  = observed temperature rise

$n$  = time in minutes between the closing of the circuit and the moment of maximum temperature

$\theta$  = average rate of cooling =  $\frac{dT}{dt}$  before the maximum temperature

$\theta'$  = average rate of cooling =  $\frac{dT}{dt}$  after the maximum temperature

This method is based on Newton's law of cooling. The differentials may be obtained from a curve.

Using the data that the heat of combustion of iron is 1,600 calories per gram and that of naphthalene 9,668 calories per gram, the water equivalent of the calorimeter can be calculated. Pure salicylic acid has been suggested as a second standard for calorimetric work for check purposes, owing to the difficulty of various workers reproducing similar results working under different conditions.<sup>1</sup> The heat of combustion of this substance is 5233.6 calories per gram weighed in vacuum.<sup>2</sup>

<sup>1</sup> *Rec. trav. Chim.*, 1930, 49, 428.

<sup>2</sup> *Ibid.* and Berner, *Rec. trav. Chim.*, 1930, 49, 861.

Using this value, the heat of combustion of other substances may be determined in an identical manner.

**The Rosenhain-Fuel Calorimeter.** In this accurate calorimeter (Fig. 14 (XI)),<sup>1</sup> which is made by the Cambridge Instrument Co., a sample of coal or an absorption pellet soaked with the oil under test is burned under water in a closed vessel. The calorimeter is an improved form of the Thomson instrument. The combustion chamber is formed from a glass lamp chimney, closed at the top and bottom by nickel-plated brass clamping plates, the joints being made by rubber washers. The sample is placed in a silica dish which stands in the bottom of the combustion chamber, and is ignited by contact with a platinum wire through which an electric current is passed. Oxygen is admitted from a cylinder fitted with a reducing valve to the

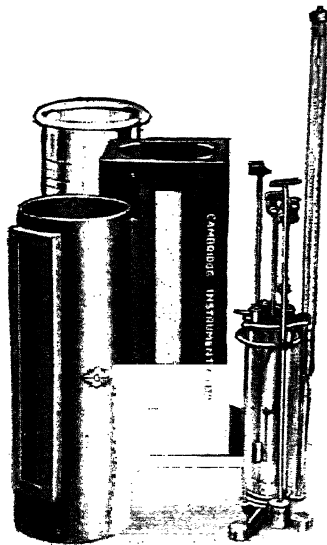


FIG. 14 (XI)

combustion chamber by means of a tube passing through the upper plate. A wire gauze nozzle is fitted to the end of this tube to prevent the oxygen jet from breaking up the coal sample. The products of combustion pass out of the chamber through an outlet fitted with a ball valve, which allows the gases to pass out but prevents the water entering the chamber. After leaving the combustion chamber the gases bubble through the water in the surrounding calorimeter vessel, and this bubbling of the gas through the water provides the stirring. An arrangement is fitted by means of which the ball can be raised to allow some water to enter. This water is then forced out by the oxygen and mixed with the rest of the water, thus ensuring that the calorimeter and its contents are brought to one temperature. The temperatures of the water are read

by means of a thermometer divided to  $0.05^{\circ}$  held in a clip on the outside of the combustion chamber. To prevent radiation the calorimeter vessel is enclosed in a wooden case, through openings in the sides of which the progress of the combustion may be watched. After leaving the cylinder the oxygen should be allowed to flow through a coil of pipe, preferably of metal, to bring it to the temperature of the room, after which it is passed through a wash-bottle. The wash-bottle should be fitted with a thermometer divided to  $0.2^{\circ}$ , and its temperature should not vary appreciably.

For standardizing the calorimeter, glass tubes, each containing four

<sup>1</sup> The block for Fig. 14 (XI) was kindly supplied by the makers.

briquettes of coal, the calorific value of which has been carefully determined, can be supplied by the firm. The water equivalent is best determined by burning in the calorimeter samples of this coal. Standardized absorption pellets for testing the calorific value of oils are also procurable. These pellets absorb a considerable bulk of liquid and burn completely and rapidly leaving no residue whatever.

The value obtained by Jessup and Green<sup>1</sup> for the heat of combustion of a standard sample of benzoic acid was 26,419 international joules per gram mass (weight corrected for air buoyancy) when the sample was burned at 25° in oxygen under an initial pressure of 30 atm. absolute under the following conditions. The burning is carried out in a bomb of constant volume, the mass of the sample and the mass of water placed in the bomb each being 3 grams per litre of bomb volume. A comparison of this result with previous high precision determinations is given in the original.

**Calorimetry.** The following table gives typical calorific values of a number of solid fuels:

	Calorific Power	
	Calories	B.Th.U.
Anthracite . . . .	8,400	15,120
Coal . . . . .	7,875	14,175
Coke . . . . .	6,900	12,420
Lignite . . . . .	4,000	7,200
Oak (13 per cent H <sub>2</sub> O)	3,990	7,182
Irish peat (air dried), <i>brown</i>	3,872	6,970 <sup>2</sup>
"    "    "    " <i>black</i>	3,878	6,980 <sup>2</sup>

For the determination of the specific heats of gases see chapter in the section on Gases.

**Determination of the Heat of Combustion of Salicylic Acid.** The experiment is carried out in exactly the same way as in the determination of the water value. 1.3 gram of the solid is a suitable quantity to weigh out. In the calculation the water value is now the known and the heat of combustion of the salicylic acid is the unknown quantity.

**Corrections in Bomb Calorimetry. Sulphuric and Nitric Acids.** These acids are not formed in combustion at atmospheric pressure, but may be produced under the higher pressure used in the bomb calorimeter, and in accurate work it is necessary to estimate them and apply a correction. For this purpose the bomb is washed out with distilled water into a beaker and the total acid is determined volumetrically; the sulphate is then estimated gravimetrically as barium sulphate.

The corrections to be applied are 227 calories per gram of nitric acid and 730 calories per gram of sulphuric acid.

**Condensation of Water in the Bomb.** When a fuel is burnt in an ordinary furnace the water formed is carried away in the form of vapour at a temperature above 100°. In the bomb this water vapour is condensed and cooled, so that, owing to the latent and specific heats, an extra amount of heat passes to the calorimeter. The gross calorific value determined must therefore be reduced by 600 calories per gram of water formed. The amount

<sup>1</sup> *J. Res. Nat. Bur. Stand.*, 1934, 13, 469.

<sup>2</sup> Donnelly and Reilly, *Sci. Proc. Roy. Dub. Soc.*, 1930, 19, 29, 365.

of water formed may be calculated as the hygroscopic water of the fuel plus an amount formed from the 'available hydrogen', or, if the Kroeker modification of the Berthelot-Mahler bomb is used without the addition of water to absorb the acids formed, the amount of water formed may be found by vaporizing and absorbing it in weighed calcium chloride tubes.

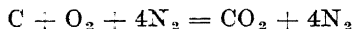
**Calculation of Calorific Values from Analytical Results.** Actual combustions give the most accurate calorific values, but by making certain arbitrary assumptions it is possible to arrive at an approximate value from the ultimate analysis of a fuel. Assume that the carbon, hydrogen and oxygen are present as elements (i.e. neglect the heat of decomposition of their compounds which may be present), and that hydrogen available for combustion is equal to the total hydrogen less an amount equivalent to the oxygen present (i.e. one-eighth the weight of the oxygen present). The calorific value  $H'$  is then given by

$$H' = \frac{34500(H - O/8) + 8137C - 600H_2O}{100}$$

here  $H$ ,  $O$ ,  $C$  and  $H_2O$  are the percentages of hydrogen, oxygen, carbon, and hygroscopic moisture respectively, and  $H - O/8$  is the percentage of 'available hydrogen'.

With simple gaseous fuel mixtures such as water gas a similar calculation is possible, but when the gas mixture is more complex it is not possible to determine the percentage of all the combustible constituents with sufficient accuracy for a calculation of the calorific value.

Another calculation often of importance in technical practice is that of the amount of air required for the complete combustion of a fuel. From the equation



it can be seen that 12 grams of carbon will require 144 grams of air and so 1 gram of carbon will require 12 grams of air; similarly, 1 gram of hydrogen will require 36 grams of air. The theoretical weight of air ( $W$  kg.) necessary for the complete combustion of 1 kg. of fuel is given by

$$W = 0.01116[C + 3(H - O/8)]$$

$C$ ,  $H$ , and  $O$  being the number of grams of carbon, hydrogen, and oxygen respectively in 1 kg. of fuel. Under working conditions the amount of air required is about  $2W$ .

It is also possible to calculate the percentage of carbon dioxide which should be present in the gases leaving the furnace, and to compare this with the actual result to obtain a check on the furnace efficiency.

**The Kroeker Bomb.** This modification of the Berthelot-Mahler bomb is very convenient in use, and particularly in the case of solid fuels when it is desirable to determine the weight of water formed. The diagram (Fig. 15 (XI)) gives a section in which the essential parts are clearly shown. With the screw  $S_2$  removed and the delivery tube from the oxygen cylinder screwed in its place, oxygen is admitted through the needle valve  $V_2$  down the long platinum tube  $R$ . With  $S_1$  removed and the valve  $V_1$  open, the air in the apparatus can be swept out if desired. When the oxygen has been admitted up to the pressure of 20 atm. the valve  $V_2$  is closed ( $V_1$

having been shut previously), and the screws  $S_1$  and  $S_2$  are replaced before the bomb is placed in the calorimeter. In closing the valves and also in

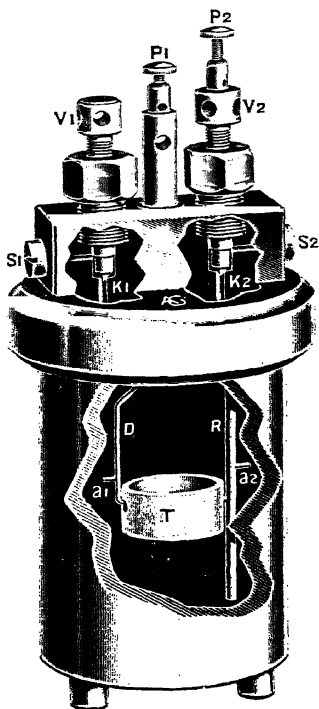


FIG. 15 (XI)

weighed out and bent so that the central part extends into the centre of the mould in which the briquette is made. About 1 gram of, for example, air-dried powdered coal is then put in the mould and pressed. The pressure on the screw is released, the plug at the bottom removed, and the briquette is forced out at the base. The wire is thus embedded in the briquette with the ends free, so that, after weighing, these ends can be joined at  $a_1$  and  $a_2$ . Allowance has to be made for the heat evolved in the combustion of the 'match'.

When the combustion is over and the necessary temperature readings recorded, the bomb is taken out of the calorimeter, the screws  $S_1$  and  $S_2$  are removed, and the nickel-plated

screwing down the lid on to the lead washer only moderate force should be used but contact surfaces and screw threads should be quite free from grit and should be smeared with a little vaseline. The platinum or quartz crucible is attached at T to the tube R and the ignition means are connected to R at  $a_2$  and the platinum pole D at  $a_1$ . Fig. 16 (XI) shows the bomb A resting in the calorimeter B, which contains the water. B is surrounded with an air jacket (with a cover H) and then by the doubled-walled vessel G containing water. The wheel E operates to give an up-and-down motion to the rod C, and to the stirrer.

When the ignition is by iron wire (0.1 mm. diameter) about 6 cm. are

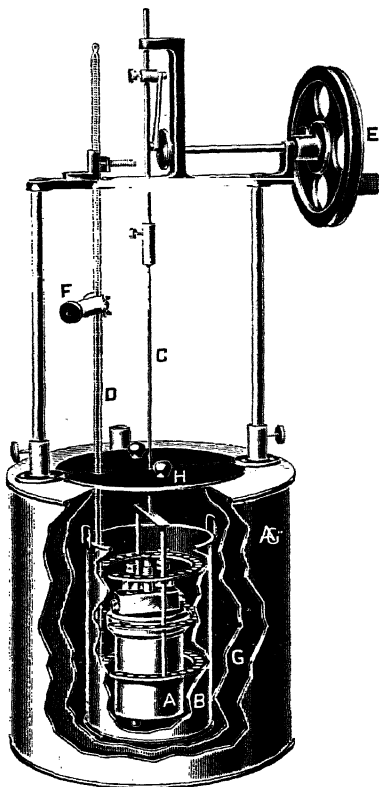


FIG. 16 (XI)

tubes provided are screwed in their places. The tube in  $S_1$  is connected to a weighed calcium chloride tube and that in  $S_2$  to a drying tower containing calcium chloride. The bomb is now placed in an air bath and valve  $V_1$  cautiously opened so that the combustion gases pass slowly through the weighed calcium chloride tube where moisture is absorbed. When the pressure has fallen to atmospheric, which requires about 30 minutes, the valve  $S_2$  is opened and dry air is aspirated slowly through the apparatus while the temperature of the air bath is raised to  $105^\circ$ . By this means, after a further period of 40 minutes, all the moisture will have been driven over into the calcium chloride tube, where it is absorbed and can be weighed.

**Example of the Calculations involved in the Determination of the Calorific Value of a Coal.** 1. *Water Equivalent of the Apparatus.* In the experiment 0.6615 gram of benzoic acid (heat of combustion 6,324 calories per gram) were burnt, using a thread weighing 0.0060 gram (H. of C. of cellulose 3,852 calories per gram); the weight of water in the calorimeter was 2,200 grams and the corrected rise of temperature observed  $1.6452^\circ$ .

Heat evolved by benzoic acid	$= 0.6615 \times 6324$	$= 4,183.3$	cal.
" " match	$= 0.0060 \times 3852$	$= 23.1$	"
Total heat evolved		$4,206.4$	"
Rise of temperature (corr.).		$= 1.6452^\circ$	
Heat required to raise temp. $1^\circ$	$= \frac{4206.4}{1.6452}$	$= 2,556.8$	cal.
Weight of water in calorimeter		$= 2,200$	gram
Water equivalent of calorimeter		$= 356.8$	cal.

2. *Method of Making the Cooling Correction.* In the experiment when the coal was burnt the following temperature readings were obtained, firing being effected at the ninth minute:

Preliminary Period			Operation in Chief	Minute	Concluding Period	
Minute	T	Minute				$d'$
0	17.766	9	17.795	12	20.231	
1	769	10	18.900	13	230	+ 0.001
2	772	11	20.140	14	228	2
3	776	12	20.231	15	225	3
4	779	3		16	223	2
5	782	3	20.231	17	221	2
6	786	4	— 17.795	18	219	2
7	789	3		19	215	4
8	792	3	2.436	20	211	4
9	795	3		21	208	3
mean cooling rate			— 0.0032			+ 0.0026

Let  $T$  = the corrected temperature rise

$T_m$  = the observed temperature rise

$n$  = time of operation in chief in minutes

$d$  = average rate of cooling in preliminary period

$d'$  = average rate of cooling in final period

$$\text{Then } T = T_m + n \cdot d' + \frac{d + d'}{2}$$

$$= 2.436 + 3 \times 0.0026 + (-0.0032 + 0.0026)$$

$$= 2.436 + 0.0077 - 0.0003$$

$$= 2.436 + 0.0074$$

$$= 2.443^\circ$$

### Calculation of the Calorific Value.

Weight of water in the calorimeter . . . . .	= 2.200 grams
Water equivalent of calorimeter . . . . .	= 356.8 "
Total water equivalent of calorimeter and contents . . . . .	<u>2,556.8</u> "
Weight of coal and cotton thread . . . . .	= 0.8343 gram
Weight of cotton . . . . .	= 0.0960 "
Weight of coal . . . . .	<u>0.8283</u> "
Corrected rise of temperature . . . . .	= 2.443°
Number of calories evolved, $2.443 \times 2,556.8$ . . . . .	= 6,246.2 cal.
Heat evolved by match $0.0060 \times 3,852$ . . . . .	= 23.1 "
Heat evolved by combustion of coal . . . . .	6,223.1
Correction for 0.4311 gram of water formed (see above), $0.4311 \times 600$ . . . . .	= 258.7
Heat of combustion of 0.8283 gram of coal . . . . .	5,964.4 "
Heat of combustion of 1 gram of coal = $\frac{5964.4}{0.8283}$ . . . . .	= 7,201 calories

In the above no correction is made for nitric or sulphuric acids formed.

Calorific values are usually expressed in British Thermal Units (1 B.Th.U. is the amount of heat required to raise the temperature of 1 lb. of water 1° F.).

$$1 \text{ B.Th.U.} = 252 \text{ cal.}$$

**Corrections for Heat Exchanges.** The corrections which have to be made for heat exchanges between a calorimeter and its surroundings have been considered by Klopsteg,<sup>1</sup> and he recommends the following method based on Newton's law of cooling. The method consists in taking temperature readings at short intervals of time, 10 or 15 seconds, before, during and after the heat input; using a graphical method to determine the rate of temperature change in the initial and final periods; using an auxiliary construction to find the average rate of change during one or more periods of time during the heat input and the corresponding time intervals and finding the correction to the observed temperature change by an algebraic summation of the product of each temperature change and its corresponding time interval.

<sup>1</sup> *J. Opt. Soc. Amer. and Rev. Sci. Inst.*, Vol. 13, 1926.



A simple case is shown in Fig. 17 (XI), where LM is the curve for the initial period. MN that during the heat intake and NO the final period: temperatures were taken each 10 seconds.

At the point A, representing the temperature  $\theta_A$ , draw the tangent to LM and so get the slope of the curve which is  $\Delta\theta_1/\Delta T_1 = R_A$ .

At the point B find  $R_B = \Delta\theta_2/\Delta T_2$  in the same way.

At the side of the diagram draw the auxiliary construction; SQ is a vertical line; horizontals are drawn from A and B to intercept SQ and lengths marked off along them from SQ proportional to  $R_A$  and  $R_B$  on any convenient scale. These distances will lie on opposite sides of SQ if the initial change was a rise and the final one a fall of temperature. Through the ends of  $R_A$  and  $R_B$  draw the line WV which in this case intercepts SQ in C.

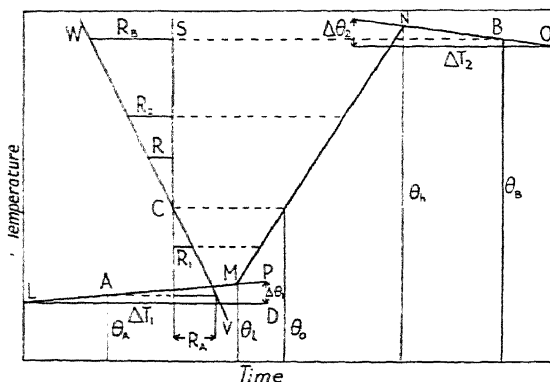


FIG. 17 (XI)

This point C represents the temperature  $\theta_c$  at which there is no heat exchange between the calorimeter and its surroundings. It is important to note that this temperature is not the same as the room temperature, it generally differs therefrom and sometimes by several degrees.

We can now correct the observed change of temperature which was from  $\theta_l$  to  $\theta_h$ . At

temperatures below  $\theta_c$  the system was gaining heat from its surroundings during the time  $t_1$  at a rate determined by the average temperature  $(\theta_c - \theta_l)/2$ ; at this temperature draw the horizontal intercept  $R_1$  to the lines SQ and WV; evaluate  $R_1$  according to the scale used and the value obtained multiplied by  $t_1$  gives the rise of temperature which occurred during the period due to heat absorbed from outside—this correction must be subtracted from the observed rise of temperature. Similarly at temperatures between  $\theta_c$  and  $\theta_h$ , heat was being lost to the surroundings. At temperature  $(\theta_h - \theta_c)/2$  mark off the intercept  $R_2$  on SQ and WV: evaluate  $R_2$  according to the temperature scale used, multiply this value by  $t_2$  to get the correction which must be added to the observed rise of temperature. The corrected temperature change is then

$$\theta = (\theta_h - t_2 R_2) - (\theta_l - t_1 R_1)$$

In case the temperature rise curve MN is not a straight line, it may be divided into a number of straight lines and the correction for each evaluated separately.

### SECTION 3: GAS CALORIMETRY

**The Calorific Value of a Gas.** This is generally measured by burning the gas at a definite rate with a special burner which is surrounded by a metal tubular coil through which water is passing. The heat of the flame is given up to the water and the increase in temperature of the latter measured. If the amount of water in the total flow is known when the temperature becomes steady the heat formed can be estimated. For practical purposes the most important form of calorimeter is that used for the estimation of the calorific value of coal gas. The Gas Referees appointed under the Gas Undertakings Acts, 1920 and 1929, in their general notification<sup>1</sup> give details of a suitable apparatus for such work. It is known as the Boys' non-recording gas calorimeter—after its inventor.

The non-recording gas calorimeter, designed by Mr. Boys in 1905, is shown in vertical section in Fig. 18 (XI). It consists of three parts: (1) the base A, carrying a pair of steatite burners B and a tap. The upper surface of the base is covered with a bright metal plate held in place by three centering and lifting blocks C. The centre of this plate is perforated and carries a ferrule W, over which is slipped a tube of fibre X, as shown. A recess 6 inches in diameter and 0.75-inch deep is turned out of the base, and a disc of felt Y, perforated in the centre, is fastened centrally in the recess. Six 0.5-inch holes Z are drilled from the corner of the recess to the groove in the base. The blocks C are so placed as to carry (2) the vessel D, which must rest only upon the horizontal portion of the blocks and be centred by their upturned ends. This vessel is provided with a central copper chimney E, and a condensed water outlet F. It is jacketed with felt R, protected by a sheet of bright metal S. Resting upon the rim of the vessel D is (3) the water circulating system of the calorimeter attached to the lid G; to this is fixed the water circulating system of the calorimeter. The water enters at O, through an inlet box which contains a thermometer. It is necessary to maintain a uniform flow of water and in the Boys apparatus there is a special overflow funnel to secure this object. The combustion products rise in the chimney E, and their heat is communicated to the water circulating in the coils. The amount is measured by the rise in temperature as indicated by the difference in readings between the thermometer O and P.

*Method of Working.* The gas is turned on and lighted and the form of the two flames observed. The flow of gas through the calorimeter is so adjusted as to allow the meter hand to make one turn in from 70 to 85 seconds if the declared calorific value of the gas is not less than 540 British Thermal Units, or in from 60 to 75 seconds if the declared calorific value is less than 540 British Thermal Units. One of the taps on the inlet side of the meter should be susceptible of fine adjustment, and the adjustment of rate must be

<sup>1</sup> Published by Stationery Office, London, 1930.

made by it, and on no account by means of the tap on the calorimeter, which must be turned on full.

The rate of gas-flow is checked by observing the time of one revolution of the meter hand with the aid of the stop-clock, stop-watch or clock with

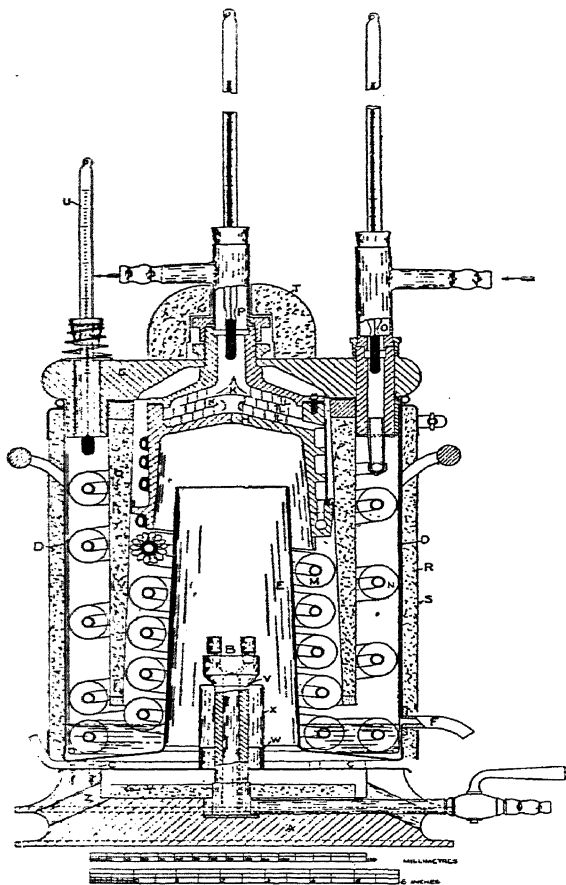


FIG. 18 (XI)

seconds hand, shortly before the temperature readings are made. The time observed is recorded.

Provision should be made to ensure that ordinarily the water entering the calorimeter is lower in temperature by not more than  $5^{\circ}$  than the surrounding air in the testing-room. The required adjustment of temperature may be effected by storing the water in a cistern in the room for several hours before a testing is made, or by heating the water passing to the calorimeter.

Heating by gas or steam, preferably subject to thermostatic control, may be employed.

The calorimeter may then be placed upon its base. The time when this is done is noted. The measuring vessel, after draining for 2 minutes, is placed in position and the change-over funnel adjusted so that the outlet water is led into the sink. The hot water outlet tube of the calorimeter should not touch the change-over funnel.

After an interval of not less than 45 minutes from the time of starting the calorimeter, the temperature of the inlet and outlet water is observed.

At every turn of the meter, except the last, a reading of the inlet temperature is made. The barometer, and the thermometers showing the temperatures of the effluent gas, of the surrounding air of the room, and of the gas in the meter, is then read.

The measuring vessel is then removed from the sink and placed upon a level surface. The water collected in the measuring vessel is thoroughly stirred and the amount read on the scale to the nearest fifth of a division. At the same time the temperature of the water is read. One of the calorimeter thermometers, preferably the outlet water thermometer, from which the cork need not be removed, may be used for this purpose. At a temperature of 15° the reading gives the weight in grammes. For higher temperatures a correction for the apparent expansion of water in glass is necessary.

The distinctive numbers of the inlet and outlet water thermometers used are noted, and after making any corrections shown on the thermometer certificates, the mean of the four readings of the inlet temperature is to be subtracted from the mean of the fifteen readings of the outlet temperature, and the difference is to be multiplied by 11.976 (which number includes a correction for the difference in the exposed mercury columns of the thermometers), by the number of kilogrammes of water collected, and by a gas volume factor. The difference in degrees in the temperature of the effluent gas and of the surrounding air is taken, and two-fifths of this difference is added to the result previously found if the effluent gas is the warmer of the two, or subtracted if the effluent gas is the cooler. The result is the number of Thermal Units (gross) produced by the combustion of 1 cubic foot of the gas measured at a definite temperature under a pressure of 30 inches of mercury and saturated with water vapour, and is the gross calorific value.

Various types of recording gas calorimeters have also been described, e.g. the Simmance's apparatus.<sup>1</sup>

**A Small-Scale Still-Water Gas Calorimeter.** An apparatus has been developed at the Newcastle Coal Survey Laboratory by means of which the calorific value can be determined on a volume of 400 ml. of gas with an error which is normally not greater than 2 or 3 B.T.U.<sup>2</sup>

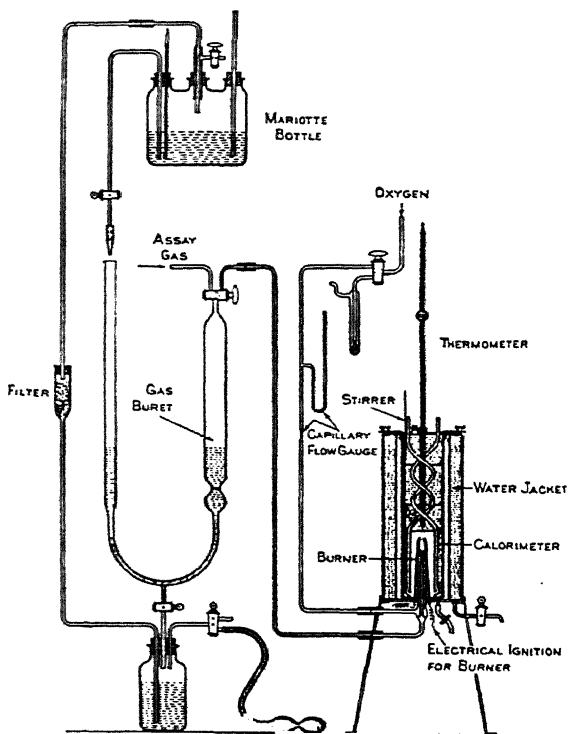
The apparatus is shown diagrammatically in Fig. 19 (XI). The calorimeter, which is of the still-water type, is constructed of copper and is mounted in an external water jacket. A measured amount of the gas to be tested is burned with only a slight excess of oxygen (thereby minimizing the volume of exit gases), using a burner with a small mixing chamber and a silica jet (0.5 mm. diameter). The exit gases deposit most of their moisture in the

<sup>1</sup> Fuel Research Board Technical Report No. 2.

<sup>2</sup> Topholme, *Ind. Eng. Chem.*, Vol. 13, No. 2, p. 26.

combustion chamber and are then conducted to the atmosphere through spiral tubes which pass through the body of the calorimeter.

The burette used for the measurement and delivery of the gas is similar to that adopted in the Fuel Research Board coke reactivity apparatus, the speed of gas passage to the burner being controlled by the rate of delivery



SCALE IN INCH

FIG. 19 (XI)

of magnesium chloride solution from the Mariotte bottle to the small diameter side limb. The use of a 20 per cent solution of magnesium chloride is found to minimize the corrections for solubility normally necessary for this type of calorimeter. The procedure is similar to the standard B.S. (British Standards) method used for determination of the calorific value of a coal, temperature readings being divided into preliminary, firing, and after periods. A temperature rise of approximately  $2^{\circ}$  is obtained with a gas of calorific value 500 B.T.U. per cubic foot, and the Regnault-Pfaundler radiation correction is applied to calculate the true rise in temperature.

The Thomas recording gas calorimeter has been described by Jessop.<sup>1</sup> The effect of changes of temperature and pressure in the readings of the calorimeter are studied. A comparison is also made between this calorimeter and one of the Junkers kind.<sup>2</sup> The Thomas calorimeter may be used to measure total heating value of gases with an accuracy well within 1 per cent.

<sup>1</sup> *J. Res. Bur. Stand.*, 1933, 10, 99.

<sup>2</sup> See Bur. Standards Circular 48, on Standard Methods of Gas Testing.

## SECTION 4: LOW TEMPERATURE PRODUCTION<sup>1</sup>

Low temperature research embraces many branches of physics and physical chemistry; the properties now being studied include density, vapour pressure, thermal capacity, latent heat, thermal and electrical conductivity, magnetism, and radiation effects.

A survey of the whole field is outside the scope of this chapter. All that is attempted here is a brief description of the production of low temperature. The measurement of low temperatures is considered in the thermometry chapter.

**Production of Low Temperatures.** The production of low temperatures is done in two ways. Up to 1933, it depended entirely on the liquefaction of gases, but in that year the new magnetic technique was developed. Some recent liquefaction methods and the magnetic methods are described here.

(a) *Liquefaction Methods.* Early successes were achieved by the Cascade process, but modern methods use the Joule Thomson effect, or the Claude expansion principle, or both.

The Joule Thomson effect depends on free expansion below a certain 'inversion' temperature.

(i) In any but perfect gases, expansion involves overcoming 'Van der Waals' attraction forces between the molecules, and a corresponding cooling.

(ii) In any but perfect gases,  $P_1V_1$  differs from  $P_2V_2$ . Assuming expansion, i.e.  $V_2$  is greater than  $V_1$ , when Boyle's Law is disobeyed so that  $P_1V_1$  is greater than  $P_2V_2$ , there will be a gain in energy in the form of heat, which may, and often does, cancel out the cooling effect of (i). But when  $P_2V_2$  is greater than  $P_1V_1$ , the gas performs external work by compressing the atmosphere, and will be cooled. In the latter case, cooling effect (i) is increased. This is generally the case at low temperatures.

The temperature at which the cooling effect due to (i) is exactly cancelled out by a heating effect due to (ii) is called the 'inversion' temperature. Obviously, liquefaction by Joule Thomson effect must be carried out below the inversion temperature.

The Claude principle depends on the fact that when a gas expands adiabatically, doing external work on a piston,

$$P_1V_1^k = P_2V_2^k$$

and since,

$$P_1V_1 = RT_1$$

and

$$P_2V_2 = RT_2$$

$$\begin{aligned} 1-k &= \frac{T_1}{T_2} \\ &= \frac{T_1}{T_2} \end{aligned}$$

<sup>1</sup> By D. J. Williams, from *School Science Review*, 1937, xix, 33.

An expansion from 100 atmospheres to 10 atmospheres should change the temperature from  $300^{\circ}$  K. to  $120^{\circ}$  K. In practice, the expansion is never quite adiabatic, and there is considerable friction, so this degree of cooling is never attained. Lubrication difficulties also make the Claude method difficult to apply at very low temperatures.

We shall describe here more recent methods which may be found in greater detail in L. C. Jackson's *Low Temperature Physics*<sup>1</sup>.

Table A gives data bearing on the liquefaction of a number of gases.<sup>2</sup>

The hydrogen liquefier at the Mond Laboratory of the Royal Society at Cambridge is a good example of the modern application of the Joule Kelvin effect.

The great difficulty to be overcome is the blocking of tubes by solid impurities in the hydrogen. Very good commercial hydrogen is about 99.5 per cent pure. Since 8.9 cubic metres of hydrogen are required for 5 litres of liquid, 19 ml. of impurity would be deposited in the tubes. In the Onnes process, the hydrogen was purified drastically before liquefaction, at considerable expense. In the Meissner process (Berlin), the apparatus was stopped periodically so that the impurities could be removed by local heating. But the liquefier at the Mond Laboratory runs continuously.

It uses two gas circuits. In one, a completely closed circuit, 0.7 cubic metres of very pure hydrogen is compressed to 170 atm. It is cooled by liquid nitrogen, boiling under reduced pressure, passes through a regenerator spiral, and then expands to normal pressure. In doing this it cools down a condenser to liquid hydrogen temperature. It then returns through the regenerator to the compressor. In the second circuit, commercial hydrogen, direct from a cylinder, has its pressure reduced to 3.4 atm. at a reduction valve. It is cooled by the liquid nitrogen and then enters the 'exchanger', which is cooled by the first circuit. Since the liquefaction temperature at 3.4 atm. is slightly higher than at normal pressure, it liquefies in the 'exchanger'. Most of the cooling takes place in this 'exchanger', and impurities will collect there and nowhere else; no stoppage is caused, and the impurities may be removed at the end of the process.

Fig. 20 (XI) shows the arrangement. 0.7 cubic metre of very pure hydrogen, compressed to 170 atm., enters at 1. It passes through the interchanger A, and through nitrogen boiling at a few centimetres pressure in B (pump at N). It continues through the regenerator D, and expands to 1 atm. at the valve E, partially liquefying in F. When F is one-third full, the liquid passes through 6, and through the coil in the condenser or exchanger G. It evaporates and passes back to the compressor via D and A. The important point is that the exchanger G is reduced to the temperature of liquid hydrogen, boiling at 1 atm., whilst the system is so efficient that the gas leaves at 2 at a temperature only slightly below that of the atmosphere.

Commercial hydrogen at 3.4 atm. is admitted at 3. It is cooled in interchanger A by outgoing pure hydrogen in 2, and by outgoing nitrogen in 5. It is cooled in the nitrogen bath B, and then goes into exchanger G, which is at the temperature of liquid hydrogen at 1 atm. Since the commercial hydrogen is at 3.4 atm., it liquefies readily and passes via 7 into F. Here

<sup>1</sup> Methuen's Monographs.

<sup>2</sup> D. J. Williams, *ibid.*

# LOW TEMPERATURE PRODUCTION

TABLE A

	Critical Temp. (° K.)	Critical Press. (Atm.)	Boiling-point. (° K.)	Temp. obtained by Evap. at Red. Press. (° K.)	Triple Point (° K.)	Latent Heat (cals. per gram.)	Sp. Heat ( $c_p$ ) at 15°	Ratio ( $c_p/c_v$ )
Argon. . . . .	150.8	48.0	87.4	—	83.8	37.6	.0746	1.666
Air . . . . .	132.4	37.2	79.2	52	—	50	.1716	1.4034
Carbon Dioxide. . . . .	304.1	72.9	194.6	—	216.7	87.2	.1534	1.302
Helium . . . . .	5.3	2.26	4.2	1	—	6.4	.7446	1.666
Hydrogen . . . . .	33.3	12.8	20.4	9	14.02	108	2.4161	1.408
Krypton . . . . .	210.6	54.2	121.4	—	—	27	.0362	1.689
Neon . . . . .	44.3	25.9	27.2	—	24.49	21	.149	1.442
Nitrogen . . . . .	126.1	33.5	77.3	50	63.3	47.6	.1759	1.405
Oxygen . . . . .	154.4	49.7	90.2	55	54.7	50.9	.1575	1.396
Xenon . . . . .	289.8	58.2	164.0	—	133	24	.023	1.666



its temperature falls to that of liquid hydrogen boiling at 1 atm., it passes out via 4 and is withdrawn at the valve H. The final cooling at F reduces the amount of evaporation when the Dewar flask is reached.

The solid impurities are removed from G at the end of the run. The whole apparatus is enclosed in an evacuated metal casing, to reduce heat absorption from the surroundings.

The liquefaction of helium offers still greater difficulties. Fig. 21 (XI)<sup>1</sup>

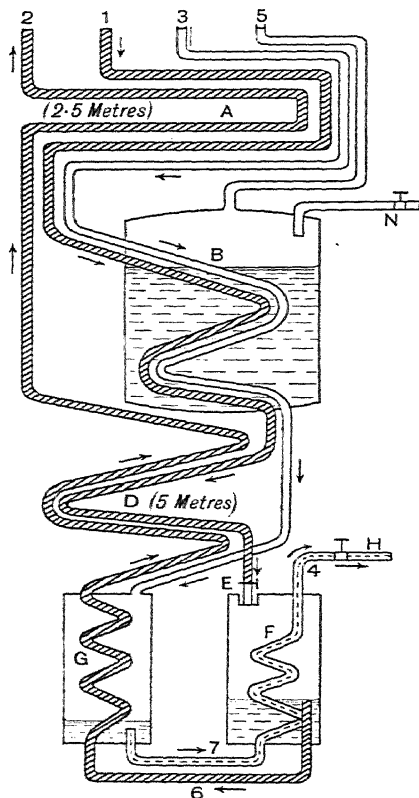


FIG. 20 (XI)

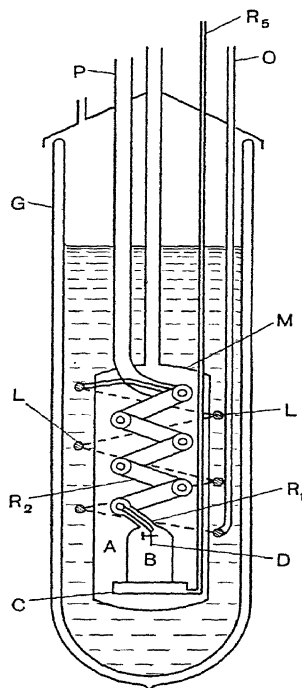


FIG. 21 (XI)

represents a comparatively simple small-scale apparatus designed by Ruhe-mann.<sup>2</sup> Very pure helium at 30/40 atm. enters at O and passes round coil L, which is surrounded by liquid hydrogen in the Dewar vessel G. This lowers the temperature below the inversion point. The helium then passes round R<sub>1</sub>, the inner tube of the exchanger A, which is contained in a vacuum vessel M. It expands to 1 atm. at the valve D, and the temperature in B is lowered

<sup>1</sup> *Zeit. f. Phys.*, 1930, 65, 67.

<sup>2</sup> Fig. 20 (XI), Fig. 21 (XI) and Fig. 22 (XI) from *School Science Review*, by courtesy of Mr. John Murray.

to  $4.2^\circ$  K., the normal boiling point of helium, in 7 minutes. Helium gas escapes into the atmosphere via the outer tube of the interchanger  $R_2$ . The temperature is measured by the small gas thermometer C, the pressure being measured through the capillary tube  $R_5$ . With apparatus small enough to fit the receiver B, experiments can be carried out down to  $1.9^\circ$  K.

The use of Claude expansion liquefiers is usually confined to oxygen and nitrogen, for the much lower temperatures required for hydrogen and helium create piston contraction and lubrication difficulties. Kapitza has, however, invented a method in which the Claude effect does most of the cooling.<sup>1</sup>

Compressed helium is cooled down to  $66^\circ$  K. in liquid nitrogen, then to  $9^\circ$  K. in an expansion engine, specially designed to overcome lubrication difficulties, and finally to  $4^\circ$  K. by Joule Thomson effect.

Fig. 22 (XI) represents a small-scale helium liquefier designed by Simon.<sup>2</sup> Activated charcoal C, freed from gas, is cooled by liquid hydrogen by conduction across the space F. Helium enters through taps 1 and 2 and is adsorbed in large quantities by the cold charcoal. The space F is evacuated to insulate the charcoal, and the helium is pumped off through taps 1 and 3. The heat of adsorption is removed, and the temperature falls below  $5^\circ$  K. Compressed helium pumped into the tube T is rapidly cooled and condenses in K. Apparatus may be enclosed in K and experiments performed down to  $2^\circ$  K. The lowest temperatures that can be produced by liquefaction methods depend on the limit to which the pressure above liquid helium can be reduced. The limit with mechanical pumps is about 0.5 mm. of mercury, and this corresponds to a temperature of  $1.2^\circ$  K., but Keesom, at Leiden, using specially designed diffusion pumps, withdrawing 675 litres per second, reduced the pressure to 0.0036 mm., corresponding to a temperature of  $0.71^\circ$  K. At this temperature the helium was still liquid. (Solid helium is obtained at a slightly higher temperature under considerable pressure.)

(b) *Magnetic Methods.* An alternative method of producing low temperatures was suggested by Debye (1926) and Giauque (1927).

A simple explanation may be rendered in terms of the Molecular Theory of Magnetism. A paramagnetic substance was to be magnetized in a strong field at as low a temperature as possible. The heat produced was to be drained off and the substance completely insulated. On demagnetizing, the tiny molecular systems would return to their original state of chaos, and, in doing so, would absorb energy. The only possible source would be the

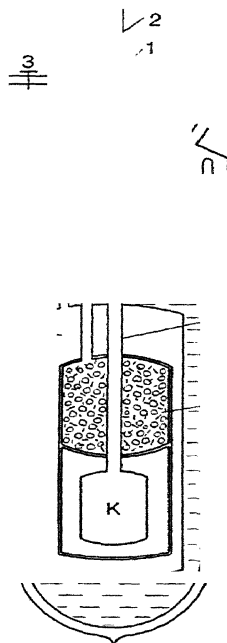


FIG. 22 (XI)

<sup>1</sup> *Proc. Roy. Soc.*, 1934, 147, 860.

<sup>2</sup> *Phys. Zeit.*, 1926, 27, 790; Mendelssohn, *Zeit. f. Phys.*, 1932, 73, 482.

kinetic energy of the molecules, and the substance would be cooled. There is a distinct analogy with a hysteresis cycle at ordinary temperatures. Iron is heated on magnetization and cooled to a smaller extent on demagnetizing.

More accurately, the entropy of the system must be considered. The change of entropy of a substance  $dQ/T$  is a measure of the change of order with regard to velocity. When a magnetic field is applied to a paramagnetic substance, the magnetic order, with respect to direction, increases. The thermal order decreases and the temperature rises. If this heat is withdrawn externally, the substance insulated, and then demagnetized adiabatically, the magnetic order decreases, the thermal order increases, and the temperature falls. Given a strong magnetic field, high susceptibility and low specific heat, the effect will be appreciable.

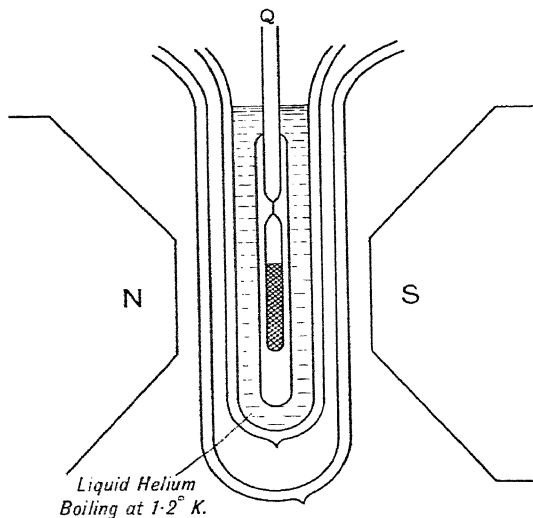


FIG. 23 (XI)

The experimental method was not perfected until 1933, but the results exceeded expectations.

Giauque and McDougall,<sup>1</sup> working with gadolinium sulphate, reached 0.25° K. Using cerium fluoride, de Haas, Kramers and Wiersma reached 0.27° K.<sup>2</sup> A little later in the same year, de Haas and his colleagues, using cerium ethyl sulphate, reached 0.085° K., and later still, using potassium chrome alum, 0.05° K. The technique was gradually improved, until finally, in February 1935, de Haas reached 0.005° K., *one two-hundredth of a degree from absolute zero*.

Fig. 23 (XI) represents approximately the apparatus used. The paramagnetic substance is enclosed in a thin tube, surrounded by liquid helium boiling under reduced pressure, the helium container, in turn, being enclosed

<sup>1</sup> *Phys. Rev.*, 1933, 43, 768; *ibid.*, 44, 235.

<sup>2</sup> *Nature*, 1933, 131, 719; *ibid.*, 1933, 132, 126.

in a specially designed 'Dewar' tube. The current is passed round the electro-magnet, and the substance magnetized in a strong field (about 30,000 gauss). The heat produced is carried away by the evaporating helium. The helium container is gradually evacuated, and the substance insulated so that it cannot gain any heat from its surroundings. The current is then switched off. The substance is demagnetized adiabatically, and cools itself. Measurements, described later, indicate that this method gives a temperature of  $0.005^{\circ}$  K.

The great failing of this method is that it cannot be used to cool other substances. Heat exchanges with the surroundings must not take place. And research at these low temperatures is producing such important results that another method is very desirable.

Simon has suggested the possibility of using a method analogous to the Claude system, substituting helium liquid for the gas which expands and does external work, but research on liquid helium has revealed unexpected properties. Meissner has shown that, if the initial temperature is below  $2^{\circ}$  K., liquid helium must be compressed in order to cool it.

## SECTION 5 : SPECIFIC HEAT OF SOLIDS

The specific heat of solids is an important quantity, not only on account of the connexion with the atomic weight (Dulong and Petit), but also in connexion with Nernst's Heat Theorem and the Third Law of Thermodynamics.

The unit of quantity of heat is the calorie which is defined as the amount of heat required to raise the temperature of 1 gram of water  $1^\circ$ . This definition is not exact, because the specific heat of water is not quite constant and the amount of heat required to raise the temperature of 1 gram of water from  $14.5^\circ$  to  $15.5^\circ$  is not quite the same as that required to raise it from  $19.5^\circ$  to  $20.5^\circ$ . There are, therefore, three different calories in use: the  $15^\circ$  calorie, when the rise in temperature is from  $14.5$  to  $15.5^\circ$ ; the  $20^\circ$  calorie, when the temperature rise is from  $19.5$  to  $20.5^\circ$ ; and the mean calorie, which is 0.01 part of the amount of heat required to raise the temperature of 1 gram of water from  $0^\circ$  to  $100^\circ$ . The last is the most definite and is greater than the  $15^\circ$  calorie by 1 part in 1,000 and exceeds the  $20^\circ$  calorie by 2 parts per 1,000. These differences will not be greater than the experimental error in the cases which follow.

The specific heat of a substance is the number of calories required to raise the temperature of 1 gram of the substance  $1^\circ$ . The specific heat is not a constant quantity but is affected by temperature: in the case of a crystalline solid, for example, it becomes zero at the absolute zero of temperature. The determination of the specific heat at a definite temperature is a matter of some difficulty, but the mean value over some definite range of temperature, for example, from  $20^\circ$  to  $100^\circ$ , can be obtained more readily.

The heat capacity of a body (sometimes called its water equivalent) is the number of calories required to heat the body  $1^\circ$ . If the body is homogeneous and its material has a specific heat  $c$ , its heat capacity  $C = m \cdot c$ , where  $m$  is the mass in grams. If it is composed of parts having different specific heats,  $c_1, c_2, \&c.$ , and  $m_1, m_2, \&c.$ , are the masses of these components

$$C = m_1 c_1 + m_2 c_2 + m_3 c_3, \&c.$$

A general method of determining the specific heat of a body is the method of mixtures. If a hot body of mass  $m_2$ , specific heat  $c_2$ , and temperature  $T_2$ , is placed in contact with a cold body of mass  $m_1$ , specific heat  $c_1$ , and temperature  $T_1$ , the hot body will lose heat to the cold one and the 'mixture' will ultimately be at the temperature  $T_3$ . The heat lost by the hot body is  $m_2 \cdot c_2 \cdot (T_2 - T_3)$ , and this is equal to the heat gained by the cold body which is  $m_1 \cdot c_1 \cdot (T_3 - T_1)$ , i.e.

$$m_2 \cdot c_2 \cdot (T_2 - T_3) = m_1 \cdot c_1 \cdot (T_3 - T_1) = C \cdot (T_3 - T_1)$$

hence, if  $c_1$  or  $C$  is known and the other quantities are measured  $c_2$  can be calculated.

In practice there is a source of error in that  $T_1$  is often the room temperature, so that the final temperature  $T_3$  is above the room temperature. The attainment of temperature equilibrium is not instantaneous, it takes time; and during this time the warm system is losing heat by radiation and conduction to its surroundings, so that the final temperature is lower than it would have been had the heat exchange been instantaneous. We attempt to combat this source of error in various ways: if one of the substances is a liquid, we use good stirring to reduce the time required for the heat exchange to be completed; if both the substances are metals their good conductivities for heat aid us. We cause the mixing to take place in an apparatus that is thermally insulated from its surroundings as far as possible; we arrange matters so that the rise of temperature above the room temperature is not great (this means that we must measure this small rise with greater accuracy); and finally, we use a radiation correction.

The way of using the radiation correction can best be explained by means of an example. The temperature of the cold body is read at intervals of 1 minute for 10 minutes at the start of the experiment: the hot body is added and the temperature measurements are continued at intervals of 1 minute for about 13 minutes more: during this time the temperature will rise to a maximum and then fall gradually. Suppose that the readings shown below were obtained with a Beckmann thermometer.

Time	Temperature $t$	Change of $t$	Time	Temperature $t$	Change of $t$	Time	Temperature $t$	Change of $t$
0	2.743	0	9	2.759	0.002	17	4.125	0
1	2.745	0.002	10	2.761	0.002	18	4.121	- 0.004
2	2.747	0.002	11	substance added	0.398	19	4.116	- 0.005
3	2.748	0.001				20	4.112	- 0.004
4	2.750	0.002	12	3.563	0.404	21	4.108	- 0.004
5	2.752	0.002	13	3.863	0.300	22	4.104	- 0.004
6	2.754	0.002	14	4.018	0.155	23	4.100	- 0.004
7	2.755	0.001	15	4.114	0.096			
8	2.757	0.002	16	4.125	0.011			

If these results are plotted on squared paper the course of the temperature changes will be demonstrated very clearly. When the rise of temperature is so small we can make the radiation correction simply as follows. The main rise of temperature was between the tenth and the seventeenth minutes and amounted to  $(4.125 - 2.761) = 1.364^\circ$ ; half this rise is  $0.682^\circ$  and the corresponding temperature is  $(2.761 + 0.682) = 3.443$ : this temperature was reached between the eleventh and twelfth minutes, and by proportion at 11.7 minutes. Had the cold body continued to warm up at the rate of  $0.0018^\circ$  per minute till this time, its temperature would have reached  $(2.761 + 1.7 \times 0.0018) = 2.764^\circ$ . If the mixture had then risen instantaneously to the final temperature  $T_3$ , and had then cooled at the rate of  $0.0042^\circ$  per minute,  $T_3$  must have had the value  $(4.100 + 11.3 \times 0.0042) = 4.148^\circ$  in order that the temperature at the twenty-third minute should be  $4.100^\circ$ . The rise would then have been  $(4.148 - 2.764) = 1.384^\circ$ , instead of  $1.364^\circ$ , which we obtained. This method of correcting for radiation will be found

sufficiently accurate for small temperature rises. Temperature corrections can also be effected by extrapolation on the time temperature graph.

**Nernst Lindemann Metal Block Calorimeter.** This calorimeter is specially suitable for the determination of the mean specific heat of solids. The heat capacity of such a calorimeter can be determined either by supplying it electrically with a known amount of heat or by the method of mixtures, in which a known mass of water at a known temperature is added to the calorimeter and the rise of temperature produced is measured. The rise of temperature can be measured conveniently by means of a multiple thermocouple (thermopile) connected to a sensitive galvanometer. Thermocouples of copper constantan are very suitable for this purpose; they give an E.M.F. of more than 40 microvolts for each degree Centigrade difference of temperature between the hot and the cold junctions: by using a thermopile of 20 junctions the E.M.F. is increased to  $800 \times 10^{-6}$  volts per degree. A suitable galvanometer consists of a microammeter having as low a resistance as possible; the change in temperature of the hot junction of the thermocouple will make a small change in the total resistance of the circuit, but this will be negligible in our case, and the current will be proportional to the E.M.F., and therefore to the temperature difference.

If the scale readings are not directly proportional to current it will be necessary to calibrate the galvanometer, but suitable microammeters can be obtained where this is not required. The soldered junctions, both hot and cold, are insulated in thin glass capillaries.

For the determination a hollow metal vessel  $M'$  is used: this is placed in the heating apparatus and raised to a temperature  $T'_2$  and is then lowered into the calorimeter. The temperature of the mixture becomes  $T'$ , and the rise of temperature of the calorimeter causes a throw of  $x'$  in the galvanometer.

Hence

$$x' \propto C'(T'_2 - T'_1)$$

$$x' = \frac{1}{K} \cdot C'(T'_2 - T'_1)$$

where  $K$  is a constant and  $C'$  is the heat capacity of  $M'$ .

The experiment is repeated with  $a$  grams of water in the metal vessel  $M'$ , the heat capacity of which therefore becomes  $C' + a$ .

If  $T_2$  is the temperature of the hot body,  $T_1$  that of the mixture, and  $x$  the throw of the galvanometer

$$x = \frac{1}{K} \cdot (C' + a)(T_2 - T_1)$$

Divide the equations all through by the fall of temperature in each case and subtract one from the other

$$\frac{x}{T_2 - T} - \frac{x'}{T'_2 - T'_1} = \frac{1}{K} \cdot (C' + a) - \frac{1}{K} \cdot C' = \frac{a}{K}$$

hence  $K$  can be determined, and this gives us the factor by which the galvanometer deflection must be multiplied to get the number of calories added to the calorimeter. Now if a body at temperature  $T''_2$  is added to the calori-

meter and  $T''_1$  is the final temperature,  $C''$  the heat capacity of the body, and  $x''$  the throw of the galvanometer produced

$$x'' \cdot K = C'' \cdot (T_2'' - T''_1)$$

hence  $C''$ , the heat capacity, can be determined, and dividing this by  $m''$ , the mass of the hot body, we can calculate  $c''$ , its specific heat.

**Determination of the Average Specific Heat of Copper (or Lead) between  $20^\circ$  and  $100^\circ$ .** The apparatus required is shown in Fig. 24 (XI).

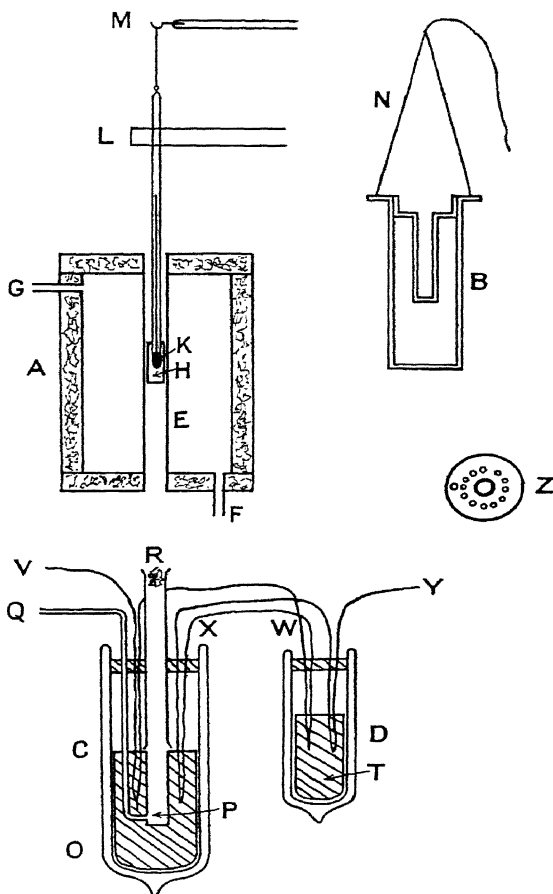


FIG. 24 (XI)

A is the apparatus for heating the solid up to a temperature in the neighbourhood of  $100^\circ$ . It consists of a cylindrical metal box with a cylindrical hole E passing right up through the centre. The outside of the box is lagged with a layer of felt to reduce loss of heat. Water is boiled in a flask or metal vessel



and the steam is passed in at the opening F and passes out through the tube G, so that the chamber E becomes heated to near  $100^{\circ}$ .

C contains the calorimeter O which is a simplified form of Nernst and Lindemann's, which is easy to construct. As will be seen from the diagram, it consists of a cylindrical block which just fits the lower half of the Dewar vacuum flask. The block is shown in horizontal section at Z. The central hole P is rather more than 1.5 cm. in diameter and is about 8 cm. deep, it has a side opening at the bottom connected to the metal pipe Q, and is surrounded by a series of holes destined to take the hot junctions of the thermocouples. The block is conveniently made of aluminium.

The Dewar flask, which is closed at the top by the perforated cork S, serves to insulate the calorimeter from its surroundings and so tends to reduce radiation errors. C is placed below A in such a position that the hole P lies vertically below E and between the two is the thin glass tube R which serves as a guide when the solid is lowered from E to P. R is plugged with cotton wool.

D is a second Dewar flask containing the block of aluminium T, which is bored with a series of holes to take the cold junctions of the thermocouples; it is closed with a cork S.

B is the hollow copper vessel used in the calibration of the calorimeter. It has a screw-on lid of the shape shown, with a cylindrical depression in the middle which is just large enough to take the bulb of the thermometer (reading to  $100^{\circ}$  in  $0.1^{\circ}$ ). B is suspended by the loop of thread N which is so long that when it is hung on the hook M, B is half-way down the tube E; at the top of the loop is a further thread long enough to lower B right down into P.

The piece of copper the specific heat of which is to be determined is shown at H; it is cylindrical, 1.5 cm. in diameter, and 5 cm. high, and it has a central hole K bored to take the bulb of the thermometer which is held in position by means of the clamp L.

VWXY show diagrammatically the arrangement of the thermocouples, V and X being hot junctions and W and Y cold junctions; V and Y are connected to the two terminals of the galvanometer.

**Carrying out the Measurement.** Start the passage of steam through the heater A and suspend the empty copper vessel M, by means of the thread N, midway down the opening E, and with the thermometer bulb in the aperture in the lid. Commence taking the galvanometer readings at intervals of 1 minute; before the tenth minute is reached it will probably be found that the thermometer in B has reached a steady value  $T'_2$ . Take the galvanometer reading at the end of the tenth minute, record  $T'_2$ , remove the cotton wool in R and, lifting the loop off M, lower B into the hole P in the calorimeter.

The thermometer will be left in the clamp. Replace the cotton wool in R and continue the galvanometer readings at minute intervals till a sufficient number has been recorded. Then take the thermometer and, when it has cooled, lower it into the hole in B in the calorimeter and record  $T'_1$ . This is not quite the correct value, because a little cooling will have occurred, but this will be very small with the apparatus used, and since  $T'_2 - T'_1$  is a large quantity a small error therein will be negligible.

Now apply the radiation correction to the galvanometer deflection in exactly the same way as it was applied in the example given above to the temperature readings: thus obtain  $x'$ , the corrected galvanometer throw.

A small refinement that may be introduced with but little trouble consists in passing a slow stream of dry hydrogen through the tube Q throughout the experiment; because of the high heat conductivity of hydrogen, temperature equilibrium will be set up more rapidly.

Repeat the experiment with a weighed quantity,  $a$  grams of water in B and so get  $T_2$ ,  $T_1$ , and  $x$  (the galvanometer throw corrected for radiation).

Finally, weigh the block of copper ( $m$  gram), repeat the procedure once more and get  $T''_2$ ,  $T''_1$ , and  $x''$ .

All the data have now been obtained for the calculation of  $C''$ , the heat capacity of the copper block and also for  $c''$ , the specific heat of the copper.

The method of Parkes<sup>1</sup> has recently been applied by Stiehler and Huffman<sup>2</sup> to determine the 'true' specific heat, entropies and free energies of a number of organic substances. The heat capacities were determined over a temperature range from 90 to 298.1° K. The method consists in supplying electrically a definite amount of heat to a gold calorimeter containing the organic substance in the form of dense pellets 2 mm. in thickness. Current and voltage measurements are made on a special potentiometer. The temperature is measured with a thermocouple. The latter is checked against a standard instrument.

The specific heat of a liquid may be obtained also by the above method if a solid of known specific heat is employed in the heater and a known amount of liquid is placed in the calorimeter. The method is straightforward and does not require detailed description. By the method of cooling or by the 'flow' method the specific heat of a liquid may be determined. For the determination of the specific heats of organic liquids at low temperatures, see *J. Chem. Phys.*, July 1937.

<sup>1</sup> *J. Amer. Chem. Soc.*, 1925, 47, 338.

<sup>2</sup> *Ibid.*, 1935, 57, 1741.

## SECTION 6: LATENT HEAT OF VAPORIZATION <sup>1</sup>

During the passage from the liquid to the vapour state a certain amount of heat is absorbed: this is called the latent heat of vaporization, and this heat is set free again when the vapour passes back into the liquid state. The latent heat of vaporization  $l$  at any temperature  $T$  is defined as the number of calories required to convert 1 gram of the liquid at temperature  $T$  into vapour at the same temperature. The term is commonly used for the special case when boiling takes place at atmospheric pressure. The molecular heat of vaporization  $L$  at a temperature  $T$  is the number of calories required to convert 1 gram molecule of liquid at  $T$  into the vapour state at the same temperature.

The latent heat is made up of two parts, firstly the work done in overcoming the external pressure and secondly that done in separating the molecules. For a gram molecule the external work is

$$A = p(v - v')$$

where  $p$  is the pressure,  $v$  the volume of a gram molecule in the gaseous state, and  $v'$  that in the liquid state; i.e.  $v$  and  $v'$  are the molecular volumes. If the pressure is not large,  $v'$  is negligible compared with  $v$ , and the external work

$$A = pv = RT = 2T \text{ calories}$$

That is the external work is independent of the nature of the liquid and depends only on the temperature. The internal work varies with the nature of the liquid.

The decrease in the total energy

$$U = RT - L$$

therefore 
$$\frac{dU}{dT} = R - \frac{dL}{dT}$$

but the rate of decrease in the total energy is equal to the difference of the molecular heats in the two states,

$$\frac{dU}{dT} = M \cdot c - C_v$$

where  $c$  is the specific heat per gram of liquid and  $C_v$  is the molecular heat of the gas at constant volume;

therefore 
$$R - \frac{dL}{dT} = M \cdot c - C_v$$

but 
$$R = C_p - C_v$$

therefore 
$$\frac{dL}{dT} = C_p - M \cdot c$$

This expression gives the rate of change of latent heat with temperature.

<sup>1</sup> See *Heat Transmission*, Part 1, Chap. 3.

Since in all cases the specific heat in the liquid state is greater than that in the gaseous state, the latent heat always decreases with rise of temperature; and this is to be expected because it must become zero at the critical temperature.

The second law of thermodynamics gives an important relationship between the latent heat of vaporization and the change of vapour pressure with temperature. If  $A$  is the external work,

$$A - U = T \cdot \frac{dA}{dT}$$

Working with 1 gram of the liquid

$$\begin{aligned} A &= p(V - V') \\ \frac{dA}{dT} &= \frac{dp}{dT}(V - V') \\ U &= p(V - V') - l \end{aligned}$$

where  $V$  is the volume of 1 gram (specific volume) of gas at pressure  $p$  and temperature  $T$ ,  $V'$  is the specific volume of the liquid and  $l$  is the latent heat per gram;

therefore 
$$l = T \cdot \frac{dp}{dT}(V - V')$$

or 
$$L = T \cdot \frac{dp}{dT}(v - v')$$

This is the well-known Clausius Clapeyron equation and enables us, for example, to calculate the latent heat from the slope of the vapour pressure curve or, conversely, to find the effect of change of pressure on the boiling-point from the latent heat.

Neglecting  $v'$  we have

$$\frac{L}{T} = \frac{dp}{dT} \cdot v = \frac{RT}{p} \cdot \frac{dp}{dT} = R \cdot \frac{d \ln p}{d \ln T}$$

according to Van der Waals the expression  $\frac{d \ln p}{d \ln T}$  should be constant at corresponding states, and Guldberg has pointed out that the boiling point at atmospheric pressure is equal to two-thirds of the critical temperature when both are measured on the absolute scale, so that boiling points at atmospheric pressure are corresponding temperatures: hence  $L/T$  is a constant when  $T$  is the boiling-point ( $^{\circ}\text{K.}$ ) at atmospheric pressure.

Trouton found that for nonassociated liquids  $L/T = 21$  (Trouton's rule). For associated liquids, such as water, greater values are obtained.

**Determination of the Latent Heat of Vaporization of a Liquid.** If the liquid boils at a temperature much above the room temperature it is usual to condense the vapour in the calorimeter and from the rise of temperature produced to calculate the latent heat of condensation. On the other hand, when the boiling-point is not far removed from room temperature a known amount of the liquid can be vaporized in a calorimeter and the cooling produced be used to calculate the latent heat of vaporization.

**Determination of the Latent Heat of Vaporization of Ethyl Ether (or Carbon Disulphide).** The apparatus in which the evaporation takes

place is shown in Fig. 25 (XI) and is due to Nernst; it consists of a glass vessel holding about 15 ml. and having an inlet tube drawn out to a fine point which reaches nearly to the bottom, and an outlet tube near the shoulder at the top. To this is connected by rubber tubing a coil of thin copper tubing which, after passing several times round the glass vessel, is continued upwards, where it is connected to a glass tube as shown. A calorimeter is required of 500 ml. capacity and provided with a jacket to reduce heat losses; the jacket consists of one, or sometimes more, polished metal vessels insulated from the first by pieces of cork, ebonite, or felt, and sometimes with the outermost jacket containing water to keep its temperature constant.

The copper calorimeter and its stirrer are weighed as are also the glass vessel and its copper spiral; the calorimeter is filled two-thirds full of water and weighed again. The heat capacity  $C$  of all this apparatus is then calculated from the masses and specific heats of its component parts.

The glass vessel is filled two-thirds full with ether and weighed, and is then connected to the copper spiral and glass tube, and to the last is attached a rubber bulb (like those used in scent sprays) for blowing a current of air through the ether. The glass vessel is fixed in the calorimeter, together with a Beckmann thermometer. The water is stirred, and readings of the temperature are made every minute—the radiation correction is most important in this case, owing to the relatively long duration of the experiment. When the temperature readings have become regular, air is gently blown through the ether with the aid of the rubber bulb; the blowing must be gentle and continuous—too vigorous blowing may cause particles of spray to be

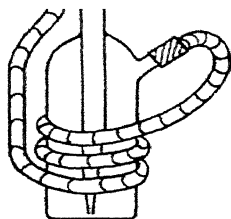


FIG. (XI)

carried right out of the apparatus without vaporizing, while a steady slow stream enables effective heat exchange to take place as the ether and air passes through the metal spiral. Readings of the temperature are continued every minute and the water is gently stirred all the time. Continue the blowing until a fall of temperature of  $0.75^{\circ}$  to  $1.00^{\circ}$  is obtained; then stop blowing, but go on taking temperature readings for another 10 minutes.

Finally, remove the glass vessel, detach the copper spiral, dry the glass and weigh it with the liquid remaining therein, and so by subtraction get  $m$ , the mass of ether which has evaporated.

Correct the temperature readings for radiation (in this case heat is gained). If the corrected temperature change is  $t$ , then

$$m \cdot l = C \cdot t$$

and  $l$ , the latent heat per gram can be calculated, and from this  $L$ , the molecular latent heat.

Use the results to verify Trouton's rule. Strictly, this is not permissible, because the latent heat has not been determined at the boiling point—if ether obeys the rule should your result be high or low?

## SECTION 7: HEAT CONDUCTIVITY OF GASES

**Definition of Conductivity.** Consider a rectangular slab of a solid. Let  $A$  be the area of the face and let the two opposite faces be maintained at constant but different temperatures. If the block is of uniform composition there will be a steady temperature gradient,  $d\theta/dx$ , from one side to the other. Heat will pass down the temperature gradient and it is found that the quantity of heat passing through is proportional to

1. the temperature gradient  $d\theta/dx$
2. the area of the face  $A$
3. the time and
4. the nature of the material

This can be represented by the equation (see page 100)

$$dQ/dt = K \cdot A \cdot d\theta/dx \quad . \quad . \quad . \quad (1)$$

$dQ/dt$  is the rate at which heat passes through in calories per second, and  $K$  is a constant for the material and is called the 'heat conductivity'.

As usual,  $K$  can be defined by making the other terms in the equation equal to unity: the conductivity thus becomes the number of calories per second passing through each square cm. of the face when the temperature gradient is  $1^\circ$  Centigrade per cm.

If instead of flowing through a plate the heat flows from the inside to the outside of a thin cylinder of length  $l$  and radius  $r$

$$dQ/dt = -K \cdot 2\pi r l \cdot d\theta/dr \quad . \quad . \quad (2)$$

(the minus sign is used because the temperature decreases as  $r$  increases).

With a hollow cylinder of finite thickness,  $r_2 - r_1$ , we can consider it to be made up of a number of concentric cylinders to each of which equation (2) will apply. The same amount of heat will flow through each cylinder and on integration we get

$$\frac{Q}{2\pi} \cdot \ln \frac{r_2}{r_1} = K l (\theta_1 - \theta_2)$$

or

$$K = \frac{Q}{2\pi l t} \cdot \frac{\ln (r_2/r_1)}{(\theta_1 - \theta_2)} \quad . \quad (3)$$

In this equation  $Q$  is the number of calories passing through in time  $t$ ,  $\theta_1$  is the temperature of the inner surface of the cylinder and  $\theta_2$  that of the outer surface, and  $\ln$  denotes natural logarithm.

**Conductivity of Gases.** The heat conductivity of a gas is an interesting property, among other reasons because of its relation to the viscosity of the gas and the related constants (see Chapter XII, Section 7, on Viscosity),

$$K = 1.603\eta C_v$$

where  $\eta$  is the viscosity of the gas and  $C_v$  is the specific heat at constant volume.

Equation (3) can be used for the measurement of the absolute conductivity of a gas in the following way: the apparatus consists of a metal cylinder of radius  $r_2$ , with a thin platinum wire of radius  $r_1$  and length  $l$  passing down its axis. A cylinder of gas of thickness  $r_2 - r_1$  is thus enclosed between the platinum wire and the metal cylinder. The wire can be heated by means of an electric current and the amount of heat supplied to the wire per second will be given by

$$Q = C^2 R = E^2 / R \text{ joules} \quad . \quad . \quad . \quad (4)$$

where  $C$  is the current in amperes,  $R$  the resistance in ohms, and  $E$  the potential difference of the ends of the wire in volts.

If the cylinder is sufficiently long for the heat losses at its ends to be negligible, when the steady state has been set up all the heat will pass from the platinum wire, through the gas to the outer cylinder which will be at room temperature  $\theta_2$ , or which can, if necessary, be kept in a thermostat to keep  $\theta_2$  constant. Everything in equation (3) is now known except  $\theta_1$ : to get this we could use a current sufficiently large to make the wire glow and its temperature could then be read with the optical pyrometer. Or, we could get  $\theta_1$  in another way: namely, by measuring the resistance,  $R_2$ , of the platinum wire at the room temperature  $\theta_2$ , using a small measuring current so that the wire was not heated appreciably and then measuring  $R_1$ , the resistance of the wire when it is heated to  $\theta_1$ , during the experiment; knowing the temperature coefficient of resistance of the platinum the higher temperature can be calculated. Relative measurements of the conductivities of two gases can be made more readily and if the absolute value for one gas is known, that for the other can be calculated. If the same apparatus is used in both cases equation (3) reduces to

$$K = \frac{Q}{(\theta_1 - \theta_2)} \cdot c$$

where  $c$  is a constant for the apparatus. If the difference between the two temperatures  $\theta_1$  and  $\theta_2$  is not too great,  $\theta_1 - \theta_2 = R_1 - R_2$ , where  $R_1$  and  $R_2$  are the resistances of the platinum wire at the two temperatures: then with the aid of equation (4)

$$K = \frac{E^2}{R_1(R_1 - R_2)} \cdot c$$

so for the two gases  $a$  and  $b$

$$\frac{K_a}{K_b} = \frac{E_a^2 \cdot R_b \cdot (R_b - R)}{E_b^2 \cdot R_a \cdot (R_a - R)} \quad . \quad . \quad . \quad (5)$$

where  $R$  is the resistance of the wire when cold

$R_a$  is the resistance with the gas  $a$  in the apparatus and the E.M.F.  $E_a$  applied, and

$R_b$  is the resistance with the gas  $b$  in the apparatus and the applied E.M.F. is  $E_b$ .

**Determination of the Heat Conductivity of Hydrogen and of Carbon Dioxide Relative to that of Dry Air at one and at one-third**

**Atmosphere Pressure.** The apparatus to be used is shown diagrammatically in Fig. 26 (XI). Pt represents a very fine platinum wire, approximately 0.03 mm. in diameter and 20 cm. long, so that its resistance is about 30 ohms. This wire is stretched between the thick copper leads ZZ along the axis of the glass cylinder AB which has the form of the outer jacket of a Liebig's condenser. The copper leads pass through rubber stoppers. The side tubes A and B serve for the introduction and removal of the gases.

This apparatus forms one branch of the Wheatstone bridge in which the other arms are the resistance box R (0 to 100 ohms) and the two sections XN and NY of the metre wire XY.

G is the galvanometer which is connected to the sliding contact at N. V is an accurate voltmeter reading 0.3 volts and connected across the ends

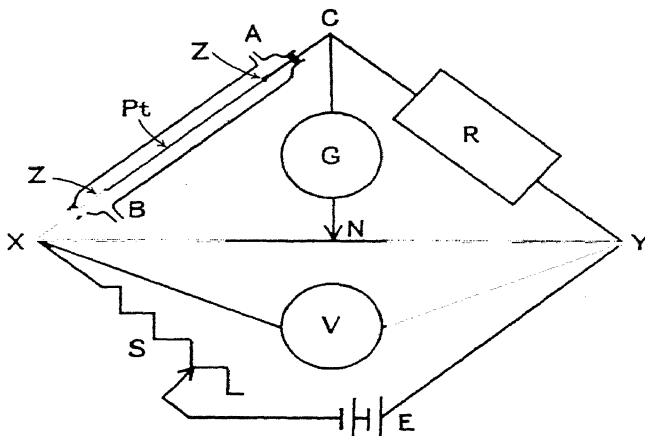


FIG. 26 (XI)

of the metre wire. E is a battery of two accumulators which is connected to the ends of the slide wire through the variable resistance S. By means of S the potential over XY can be varied, and by means of V the value of this potential difference can be measured.

In making the connexions take particular care to clean all contacts thoroughly with sandpaper. The plugs in the resistance box should also be cleaned and then given a covering with a film of oil.

The first step is to measure R, the resistance of the platinum wire at the room temperature; for this purpose a low voltage is used across XY so as to avoid heating effects in Pt. Resistances are put in from R until a point of balance N is obtained near the centre of the wire; now

$$R_{Pt} = R = R_R \cdot XN/NY$$

The potential difference XC is equal to that for XN and

$$E_{XN}/E_{XY} = XN/XY = E_{XN}/V = E_{XC}/V$$

so that

$$E_{XC} = V \cdot XN/XY$$



Ensure that too high a voltage has not been used by raising the voltage a little and verifying that the balance is not altered.

Next, fill the apparatus with pure dry air at atmospheric pressure: the air is purified by passing through concentrated caustic potash solution and then over calcium chloride and phosphoric anhydride.

Gradually increase the voltage until a suitable change in the resistance of Pt has been produced. Balance this resistance as near as possible by means of the resistance box R and complete the adjustment with the sliding contact N until no current flows through the galvanometer. Calculate  $R_a$ , the resistance of the platinum wire and  $E_a$ , the E.M.F. applied, as shown above. Repeat the determination of R and  $R_a$  a second time.

By means of a water pump and a manometer reduce the pressure in the apparatus to 0.33 atmosphere and make two further determinations: call the values obtained  $R_b$  and  $E_b$ . Substitute the two sets of values in equation (5) and compare the heat conductivities at the two pressures.

What conclusions can you draw as to the effect of pressure on the viscosity of a gas?

Replace the air in the apparatus by pure dry hydrogen, best by repeated evacuation and filling. Measure  $R_b$  and  $E_b$ , using about the same value for the voltage V as before. Use equation (5) to get the conductivity relative to air.

The conductivity of air has the values

at 0°	$5.33 \times 10^{-5}$	calories	per cm.	per degree	per second
10°	$5.48 \times 10^{-5}$	"	"	"	"
20°	$5.63 \times 10^{-5}$	"	"	"	"

so that the absolute value for hydrogen can be calculated.

Repeat the experiment, using carbon dioxide.

#### **Analysis of Gas Mixtures by the Heat Conductivity Method.**

This method has been shown by Hurst and Rideal<sup>1</sup> to be a very sensitive one: they state that using quantities as small as 1.3 c.mm. at atmospheric pressure, admixture of hydrogen and carbon monoxide could be determined within 0.05 per cent.

The method has now become a technical one and an automatic recording instrument based on this method for the control of flue gases is in use.

The principle of the method is this: suppose we have two identical pieces of apparatus like that described in the last section and the resistances of the wires are denoted by  $R_1$  and  $R_2$  where  $R_1 = R_2$ . Let these two wires form two arms of a Wheatstone bridge and let the other two arms be formed of two equal resistances  $r_1$  and  $r_2$  of about the same magnitude as  $R_1$  and  $R_2$ .

If both the tubes contain the same gas and  $R_1 = R_2$  and  $r_1 = r_2$  at room temperature, there will be the same equivalence at high temperatures because each piece of apparatus is supposed to be identical, each contains a gas of the same heat conductivity, each wire is heated to the same temperature and so increases in resistance to the same extent. The galvanometer will therefore show no change.

Now let a gas of slightly different conductivity be placed in one tube; for example, let it be a mixture of the first gas containing  $p$  per cent of a

<sup>1</sup> *J. Chem. Soc.*, 1924, 125, 694.

second gas and let its conductivity be slightly lower than that of the first gas. When the same voltage as before is applied the wire in the second apparatus will rise to a higher temperature because the heat is conducted away more slowly : the resistance of this wire will be greater than that of the wire in the first apparatus ; that is,  $R_2$  will be greater than  $R_1$  ; but  $r_2$  still equals  $r_1$ , so that now F and N are no longer at the same potential and a current will flow through the galvanometer.

If we take care that the voltage remains constant, the current in the galvanometer will be directly proportional to the small change of resistance in  $R_2$  and this again is proportional to the difference in conductivity of the gases and to the proportion of the second gas.

If the deflections in the galvanometer are proportional to the current we have

$$p'/p'' = a'/a''$$

where  $p'$  and  $p''$  are the percentages of the second gas in the mixture and  $a'$  and  $a''$  are the deflections produced in the galvanometer.

**Determination of the Percentage of Carbon Dioxide in a Mixture of Air and Carbon Dioxide.** The necessary apparatus is shown in Figs. 27 (XI) and 28 (XI). On the left is the vessel to contain the gases.

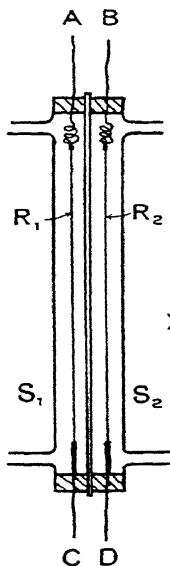


FIG. 27 (XI)

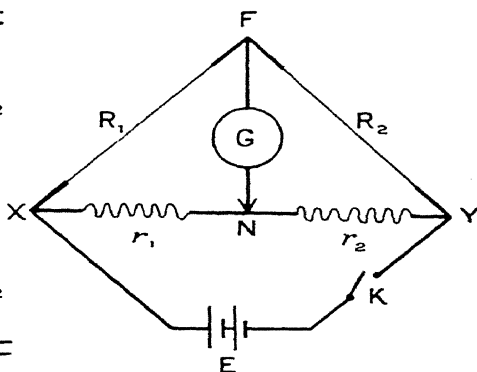


FIG. 28 (XI)

It is a cylinder of copper divided symmetrically into two compartments  $S_1$  and  $S_2$ , one of which is to contain the mixture and the other the comparison gas, in this case air.

AC and BD are the thick leads which have the thin platinum wires  $R_1$  and  $R_2$  stretched between them : in order to keep these wires taut when they

are hot, there is a spiral of thick German silver wire at the upper end. The wires are 20 cm. long and have a resistance of 8 or 9 ohms (S.W.G. 46). The leads A and B are connected as shown at F to the galvanometer. C and D are joined by way of two 10-ohm coils,  $r_1$  and  $r_2$ , to the ends of the slide wire of the bridge N. The battery E consists of two accumulators and may be connected to a variable resistance (not shown) and the key K. G is a microammeter, so that one scale division is equal to  $10^{-6}$  amps.

*Measurement.* With air in both  $S_1$  and  $S_2$  move the sliding contact N along the slide wire until the point of balance is found and no current passes through G.

In a gas-holder containing a concentrated common salt solution, prepare a mixture containing approximately 10 per cent of carbon dioxide in air. Evacuate  $S_2$ , fill with the mixture, evacuate again and refill. Now, on passing the current the galvanometer should show a deflection; increase or decrease the current until the deflection has a convenient magnitude  $a'$ , and record this.

Analyse a specimen of the gas mixture by means of a gas absorption pipette containing 40 per cent potash and so obtain  $p'$ , the percentage of carbon dioxide.

Repeat the experiment with a gas mixture containing about 20 per cent of carbon dioxide, using the same current as before, and get  $a''$ , the deflection in the galvanometer; now calculate  $p''$ , the percentage of carbon dioxide in the mixture from the expression

$$p''/p' = a''/a'$$

Verify the correctness of the result by an analysis of the mixture.

**Analysis of Gas Mixtures containing a Small Proportion of a Combustible Gas.** If the gas mixture consisted, for example, of nitrogen containing a small percentage of oxygen, and we added to this a little hydrogen, more than enough to combine with all the oxygen, and then passed the mixture over a platinum wire at a temperature in the neighbourhood of  $400^\circ$ , the platinum would act as a catalyst for the combination of the hydrogen and oxygen, this reaction would produce heat on the surface of the platinum wire, causing it to rise in temperature and so to increase in electrical resistance. Oxygen containing a little hydrogen, hydrogen containing a little oxygen, or flue gases containing unburnt carbon monoxide and oxygen would produce a similar result without the addition of another gas.

When the amount of the combustible gas is small the rise of temperature produced is practically proportional to the percentage of the gas present. The increase in the resistance of the wire is approximately proportional to the rise of temperature so that measurements of the resistance of the wire can be used to determine the gas quantitatively after the apparatus has been calibrated by means of gas mixtures of known composition.

**Determination of the Oxygen Content of Commercial Compressed Nitrogen.** Commercial nitrogen prepared from liquid air always contains a small percentage of oxygen, less than 2 per cent.

The apparatus required is similar to that shown in Fig. 26 (XI), with certain modifications. It will be remembered that the wire Pt has a resistance of about 40 ohms when hot, the balancing resistance R will also be about

40, so that we shall require the battery E to give about 40 volts in order to produce the current of 0.5 amps. which is found to be necessary to heat the platinum wire Pt up to  $450^{\circ}$ . This current is much too large to pass through the ordinary resistance box, so that R is replaced by a sliding rheostat which is capable of carrying the current. The regulating rheostat R must also be capable of dealing with the current used, and the voltmeter V will have a range up to 40 volts. Finally, the wires XN, NY are replaced by two high-resistance coils of, say, 1,000 ohms.

The gas mixture is made up in a gas holder and between this and BA is the following piece of apparatus; a glass T-tube with a tap on each arm and with the two arms bent parallel to each other; to one arm is connected by means of a rubber tube a piece of combustion tube 1.5 cm. in internal diameter and 30 cm. long; this tube contains platinized asbestos and can be heated with a Bunsen burner; the other arm of the T-tube is connected to an empty glass tube, also 30 cm. long, and the two free ends of these tubes are connected by rubber tubing to a second T-piece and then to B. By this means gas from the gas holder can be passed to the apparatus BA either through the empty tube or through the tube containing the platinized asbestos.

The first step is to make up the mixture in the gas holder: for this purpose the latter is filled with water and then nitrogen from the cylinder is slowly passed in, while the water which is at the same time driven out is collected and measured, taking care that the final pressure is atmospheric. When about 10 litres of nitrogen have been introduced, hydrogen from a Kipp's apparatus is added until the mixture contains from 5 to 10 per cent; this volume is also obtained from the volume of the water. We shall require to know later on how much gas has been used, we can measure this by using a measured volume of water to drive it out.

Heat the hard glass tube containing the platinized asbestos by means of a Bunsen burner and pass the gas mixture slowly by this path into BA; as the gas passes over the hot platinized asbestos the oxygen is catalytically burnt to water, so that the gas mixture reaching BA is free from oxygen. Now, using the smallest possible measuring current so as to avoid heating the wire, measure the resistance,  $r_t$ , of the wire Pt at the room temperature, the rheostat being replaced by the resistance box R. Stop the flow of gas and calculate what will be the resistance,  $r_x$ , of Pt at  $450^{\circ}$  by the use of the formula

$$r_x = r_0(1 + 3.39 \times 10^{-3}t - 5.8 \times 10^{-7}t^2)$$

where  $r_0$  is the resistance at  $0^{\circ}$  and  $t$  is the Centigrade temperature.

Replace AB by the rheostat and, with the aid of the resistance box, set the rheostat so that its resistance is equal to the calculated resistance  $r_x$ . Put the rheostat in place of R and replace the tube BA. Pass the gas mixture over the platinized asbestos and then into the tube BA and gradually increase the current from E until the wire Pt is at  $450^{\circ}$  as is shown by the deflection of the galvanometer G falling to zero. Change over the path of the gas mixture so that it no longer passes over the platinized asbestos but goes along the empty tube to B, which it now enters containing  $p$  per cent of oxygen. Catalysis occurs on the wire Pt which thereby becomes heated to a still higher temperature, with a corresponding increase in its electrical

resistance : this destroys the balance of the bridge, and the galvanometer G shows a deflection of  $n_1$  scale divisions. The volume of gas used must now be measured (from the volume of water which has been allowed to enter) so that the volume of gas remaining can be calculated. Allow a carefully measured volume of oxygen to enter, so that the percentage of this gas is increased by about 1 ; call this  $a$  per cent, so that the total percentage of oxygen is now  $p + a$  calculated on the original gas, i.e. omitting the hydrogen. Let this gas mixture pass through BA at the same rate as before and measure the new deflection,  $n_2$  scale divisions of the galvanometer ; then

$$\frac{p}{p + a} = \frac{n_1}{n_2}$$

or

$$p = a \cdot \frac{n_1}{n_2 + n_1}$$

## CHAPTER XII

### OTHER PHYSICAL MEASUREMENTS

#### SECTION 1: TRANSITION POINTS

THE methods which have been used to determine transition-points are <sup>1</sup>:

1. *The dilatometric method.* This depends on the difference of density of the two forms.

2. *The solubility method.*

3. *The thermometric method.* This depends on the heat change which accompanies the transformation, corresponding to the latent heat of fusion of a pure solid.

4. *The vapour-pressure method.*

5. *The electrical conductivity method.* This depends on the fact that curves for the conductivity of saturated solutions of the two forms intersect at the transition-point.

6. *The E.M.F. method.* At the transition temperature the E.M.F. of a cell will be zero when the elements consist of saturated solutions of the two forms.

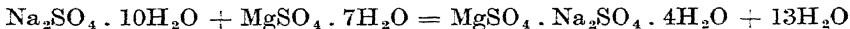
7. *Viscosity of solutions method.*

8. *Optical methods.*

1. **The Dilatometer Method.** This was used by Van't Hoff in his early determinations of transition temperatures.

*The apparatus.* A diagram of this is shown in Fig. 1 (V). The cylindrical bulb A has a capacity of about 40 ml., and to this is sealed a capillary tube B of 0.5 mm. bore and a wider tube C.

*Example.* As an example of the use of the dilatometer the case of astrakanite may be taken:



At temperatures above 21.6° the double salt is stable and below 21.6° the two simple salts. The dilatometer is inverted and a glass bead is dropped in to close the entrance to the capillary. The two salts, having been purified by recrystallization, are ground up separately and then thoroughly mixed in the proportions required by the equation. The mixture is placed in the bulb of the dilatometer so as to fill it three-quarters full and the end C is sealed. The dilatometer after cooling is inverted and filled with a suitable liquid. When the transformation does not occur readily it is an advantage

<sup>1</sup> For nature of Transition Point, see page 171.

to use a liquid which dissolves the solid to some extent, but, of course, the liquid used must not dissolve in the substance under examination, since this would lower the transition temperature. In the present case, benzene, toluene or xylene can be used. The top of the capillary B is passed through the cork in an adapter and the liquid to be used is placed in the latter. The adapter is attached to the pump and the air removed from A as completely as possible; on releasing the pressure the liquid in the adapter is forced down into A. The process is continued until all air bubbles have been removed and the meniscus of the liquid is in B. The level of the meniscus is then brought near the bottom of B by passing a finely drawn-out capillary of glass down the bore. A millimetre scale is wired on to the tube B. The dilatometer is placed in a large beaker of water at about  $16^{\circ}$  and left for 10 minutes for temperature equilibrium to be reached, and the position of the meniscus on the scale is read. The temperature is slowly raised to  $17^{\circ}$  and maintained there for 10 minutes; both the solid and the liquid expand so that the meniscus rises in B; the new position is read and the process repeated at intervals of  $1^{\circ}$  until  $25^{\circ}$  is reached. When the transition temperature is reached the solid changes into the new form and this is usually accompanied by a volume change which makes itself apparent in the readings, as shown in Van't Hoff's results with astrakanite.

Temperature	Level of liquid in B	Rise per 1
$15.6^{\circ}$	. 134	—
$16.6^{\circ}$	. 141	7
$17.6^{\circ}$	. 148	7
$18.6^{\circ}$	. 154	6
$19.6^{\circ}$	. 161	7
$20.6^{\circ}$	. 168	7
$21.6^{\circ}$	. 241	73
$22.6^{\circ}$	. 243	2
$23.6^{\circ}$	. 251	8
$24.6^{\circ}$	. 259	8

The transition-point is therefore near  $21.6^{\circ}$ . The thermostat can then be cooled at intervals of  $1^{\circ}$  and a new value of the transition-point found. This will usually be below the first value. The difference between the values found with falling and rising temperatures can then be narrowed down by increasing the time during which the temperatures are maintained. A second method depends upon the fact that both forms can coexist without change at the critical temperature. This method was used by Reicher to determine the transition-point of sulphur under pressure. The bulb was filled with a mixture of rhombic and monoclinic sulphur, and after the end C was sealed, A was filled with a mixture of 1 part of carbon disulphide and 5 parts of turpentine. The top of B was sealed off so that the pressure in the apparatus at the transition-point was the vapour pressure of the mixed liquids, namely 4 atm. The dilatometer was first maintained in a bath at  $95.1^{\circ}$ , when a gradual contraction was observed due to monoclinic sulphur passing into rhombic. With the bath at  $96.1^{\circ}$  expansion occurred owing to the reverse change. At  $95.6^{\circ}$  no volume change occurred, so this is the transition-point. The actual figures obtained were:

95.1°		96.1°		95.6°	
Time in minutes	Level of liquid	Time in minutes	Level of liquid	Time in minutes	Level of liquid
5	343.5	5	342.75	5	368.75
30	340.5	30	354.75	100	368
55	335.75	55	360.5	110	368.75
65	333	65	361.5		

In this case the transformation is slow and the second method gives more satisfactory results.

**2. The Solubility Method.** The solubility of the two forms is the same at the transition-point, so that the solubility curves of the two forms will intersect at this point. Goldschmidt used the apparatus shown in Fig. 1 (XII) for determinations of solubility. The solute, say sodium sulphate, is placed in the tube and is stirred with the solvent water by means of the Witt stirrer. When the solution is saturated the rod *f* is pulled up, whereby the solution is allowed to flow down the tube *c* where the undissolved solid is filtered out by the plug of cotton wool at *d*. If necessary, suction can be applied at *e*. The apparatus is now removed from the thermostat and the vessel containing the solution is stoppered, dried and weighed. The water is then driven off and the solid heated to constant weight at 110°, whereby the solubility is obtained. During the saturation the whole apparatus is immersed in the thermostat, and in the case of sodium sulphate separate determinations can be carried out at 28°, 30°, 32°, 34°, 40° and 45°. When the solubilities are plotted they will be found to lie on two curves which intersect at 32°. The nature of the solid present in equilibrium with the saturated solution should be determined by removing a portion, drying it as rapidly and completely as possible between filter paper, and determining the water of crystallization by heating to constant weight at 110°. This is particularly necessary because it is possible to obtain metastable saturated solutions beyond the transition-point. This is shown in the following tables:



FIG. 1 (XII)



Sol. of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		Sol. of $\text{Na}_2\text{SO}_4$	
Temperature	Solubility	Temperature	Solubility
0°	5.02	18°	53.25
10	9.00	25	51.53
20	19.40	30	50.37
25	28.00	33	49.71
30	40.00	34	49.53
33	50.76	36	49.27
34	55.00	40-15	48.78

**3. Thermometric Method.** This method has been very carefully studied by Richards and he finds that the transition-points of such systems as  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{solution}$  are sufficiently definite to be used as fixed points in thermometry. The apparatus used is similar to that used by Beckmann for the freezing-point determination, consisting of two test tubes one within the other, immersed for nine-tenths of their length in a thermostat. The inner tube is 3.3 cm. in diameter and 16 cm. wide (capacity about 120 ml.). The inner tube is separated from the outer by a narrow rubber ring, and is closed by a rubber stopper through which pass two glass tubes: one of these serves to hold the thermometer, which is kept in position by a piece of rubber tube, and the other glass tube admits the platinum stirrer. Sodium sulphate was found to be purified sufficiently by two recrystallizations. About 50 grams of the decahydrate are powdered and placed in the tube; the latter is then heated to 33°, so that it partially melts; a little anhydrous sodium sulphate is added, the thermometer and stirrer are inserted in the pasty mass, and the two test tubes (which in the meantime have cooled down) are placed in the thermostat maintained at 33°. The pasty mass is stirred gently and temperature readings are taken every minute. At the transition-point the temperature remains constant for a considerable time. The transition-points of some systems determined by this method are given by Richards and Yngve.

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	$\rightleftharpoons \text{Na}_2\text{SO}_4 + \text{soln.}$	32.383°
$\text{NaBr} \cdot 2\text{H}_2\text{O}$	$\rightleftharpoons \text{NaBr} + \text{soln.}$	50.674°
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	$\rightleftharpoons \text{MnCl}_2 \cdot 2\text{H}_2\text{O} + \text{soln.}$	58.089°
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	$\rightleftharpoons \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{soln.}$	61.341°
$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	$\rightleftharpoons \text{SrBr}_2 \cdot 2\text{H}_2\text{O} + \text{soln.}$	88.62°

**4. The Vapour-pressure Method.** At the transition-point the vapour pressures of the two forms of the substance are identical, while at any other temperature that of the unstable form is greater than that of the stable form. The Bremer Frowein tensimeter can be used to compare the vapour pressures of the two crystalline hydrates of a substance. The apparatus is shown in Fig. 2 (XII). The two flasks F,  $F_1$  and the tube  $h$  are open at the top. To determine the transition-point of sodium sulphate the procedure is as follows: some of the decahydrate is powdered and mixed with a little of the anhydrous salt. The mixture is put in the small flask F; in  $F_1$  is put some powdered decahydrate and a few drops of a saturated solution of this salt; F and  $F_1$  are then sealed. By means of the tube  $h$  olive oil or  $\alpha$ -bromo-naphthalene is introduced so as to fill the manometer A half full. The apparatus is then placed flat so that the liquid runs into the tubes  $a$  and  $b$  and the whole apparatus is exhausted through  $h$  by means of

a mercury pump, and  $h$  is sealed. When the apparatus is placed vertically the oil runs back into the manometer and its difference of level registers the difference of the vapour pressures of the systems in  $F$  and  $F_1$ . Place the apparatus in a thermostat at  $30^\circ$  and read the manometer levels from hour to hour. When the reading becomes constant record it and raise the temperature of the thermostat to  $31^\circ$ ; repeat the observation. As the temperature is raised  $1^\circ$  at a time the difference of level will be found to become less and less until at the transition-point it is zero.

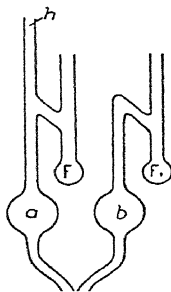


FIG. 2 (XII)

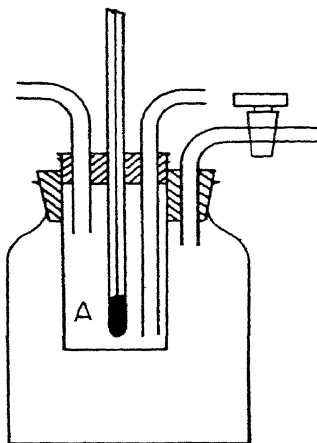


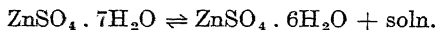
FIG. 3 (XII)

Cumming<sup>1</sup> describes a dew-point method using the apparatus shown in Fig. 3 (XII).  $A$  is a silver thimble 2 cm. in diameter, 10 cm. long, fitted at the top with a three-holed cork carrying a thermometer and two glass tubes. The apparatus containing the system of which the vapour pressure is to be determined is placed in the thermostat for some hours. Ether is placed in  $A$  and air is slowly bubbled through so that the temperature of the ether and also that of the thimble falls very slowly. As soon as dew is seen to be deposited on the silver surface the air current is stopped and the temperature read. The ether then slowly warms up, and when the last trace of mist on the silver disappears the temperature is again read. The mean of the two temperatures is taken as the dew-point. The aqueous vapour pressure corresponding to the dew-point can be determined. Determinations are then made at other temperatures and with other forms of the substance; the vapour-pressure curves will intersect at the transition-point.

<sup>1</sup> *J. Chem. Soc.*, 1909, 95, 1772.

**5. The Electrical Conductivity Method.** In certain cases, where the transformation of one hydrate into the other takes place with extreme slowness, the transition-point can be determined by measuring the conductivities of saturated solutions of the two forms over a range of temperatures which includes the transition temperature. When the two curves for conductivity against temperature are plotted they will intersect at the transition temperature, because at any other temperature that form which is unstable will have the greater solubility and therefore the greater conductivity. This method was used by Cohen for the two hydrates  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ . The hydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  is obtained by recrystallization at room temperature. Cohen prepared the hexahydrate by covering a solution saturated at  $60^\circ$  with a layer of paraffin oil, and allowing it to cool slowly in a large water-bath. The transition-point is  $39^\circ$ . Saturated solutions may be prepared in the ordinary way by shaking the powdered salts with water at a series of temperatures between  $30^\circ$  and  $45^\circ$ , and the conductivities of the solutions may be determined at these temperatures by the ordinary methods. Dipping electrodes can be used conveniently and resistances can be plotted directly against temperatures.

**6. Electromotive Force Methods** may also be used in those cases when the transition from one form to another does not take place too readily. Several modifications of the method have been used. Callendar and Barnes found the transition-point of



by making up Clark cells, in which the elements are mercury in mercurous sulphate and zinc in zinc sulphate, and measuring the E.M.F.s at different temperatures. When the zinc was in contact with a saturated solution and crystals of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , it was found possible to make measurements from  $20^\circ$  up to a few degrees above the transition-point ( $39^\circ$ ), while in a cell in which the zinc was in contact with a solution and crystals of the hexahydrate measurements were made from  $46^\circ$  down to the freezing-point. When the E.M.F.s of the two cells were plotted against temperature the curves crossed at the transition-point.

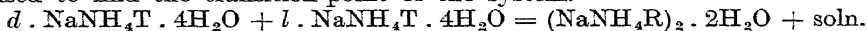
Cohen used a form of dilution cell for the same purpose. If the two elements of a cell both consist of zinc in zinc sulphate solution an E.M.F. is obtained if the zinc sulphate solutions have different concentrations. If, therefore, the solutions are saturated with hexahydrate and heptahydrate respectively, the saturated solutions will have different concentrations at all temperatures other than the critical temperature. At temperatures below  $39^\circ$  the hexahydrate, being the metastable form, has the greater solubility, and therefore its saturated solution has the greater concentration; consequently in this case a current will flow from the heptahydrate to the hexahydrate in the cell. Above  $39^\circ$  the reverse will be the case, and at  $39^\circ$  the E.M.F. will be zero. A form of cell convenient for the measurement is shown in Fig. 4 (XII), the two halves of the cell being separated by means of the tap. The tap is closed and a saturated solution, together with some finely powdered hexahydrate, is placed in one limb, while saturated solution and powdered crystals of heptahydrate are placed in the other. The tap is opened and the apparatus tilted to remove the air bubbles from the bore of

the tap, which is then closed and the stoppers carrying the zinc rods are placed in position. The apparatus is placed in a thermostat at  $25^{\circ}$  and kept there for half an hour with occasional shaking to assist the attainment of saturation. The E.M.F. is measured after opening the tap and is repeated after 15 minutes to ensure that saturation has been reached. The tap is kept closed except during measurements to prevent the mixing of the solutions. The measurements are then repeated at intervals of about  $5^{\circ}$  up to  $50^{\circ}$ . The E.M.F. will be found to become zero at  $39^{\circ}$ , and thereafter to change in sign.

Cohen and Bredig used a saturated solution of zinc sulphate in contact with the solid in one element and an unsaturated solution in the other. In this case, when the E.M.F. is plotted against temperature, a distinct break occurs in the curve at the transition-point.

Cohen also used the E.M.F. method to find the transition-point of the system grey tin and white tin ( $20^{\circ}$ ). When two different metals are placed in the same solution an E.M.F. is set up, and the same is found to be true when two different forms of the same metal are placed in one and the same solution. Thus, with white tin and grey tin as the electrodes in a 10 per cent solution of ammonium stannic chloride (pinksalz) at  $5^{\circ}$ , an E.M.F. of a few millivolts is set up. At  $20^{\circ}$  this E.M.F. is zero and above  $20^{\circ}$  it is reversed. Below  $20^{\circ}$  the white tin is the metastable and the grey tin the stable form. The metastable form always has the higher vapour pressure and the greater solubility; in this case therefore a larger potential difference will be set up between the white tin and the solution than between the grey tin and the solution, and so the E.M.F. between the two forms of the metal is set up. At the transition-point both forms are stable and have the same solubility, so that the same potential is set up between each form of the metal and the solution and the cell as a whole gives no E.M.F. Above  $20^{\circ}$  the grey tin is the metastable and the white tin the stable form, so that again an E.M.F. is set up, but in the opposite direction to that obtained at  $5^{\circ}$ .

**7. Viscosity Methods.** Dunstan and Thole showed that both the density and viscosity of solutions of sodium ammonium tartrate could be used to find the transition-point of the system.



The ordinary methods of determining the viscosity and density were used, and both these quantities when plotted against temperature gave curves showing a break at the transition-point ( $28.3^{\circ}$ ). An example of their results for a solution containing 25.19 grams of the tetrahydrate in 100 grams of solution is shown in the following table:

Temperature	Time of flow in seconds	Density	$t \times d$
25° . . . . .	438.3	1.1085	485.9
26 . . . . .	428.2	1.1081	474.4
27 . . . . .	418.4	1.1077	464.5
28 . . . . .	410.3	1.1072	454.3
29 . . . . .	402.6	1.1068	445.6
30 . . . . .	392.3	1.1064	434.0

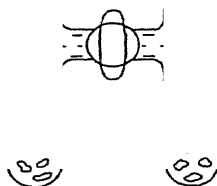
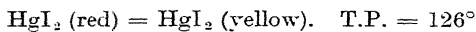


FIG. 4 (XII)

8. **Optical Methods.** Some systems show a change in colour at the transition-point. We have, for example,



and this change can be observed by directly heating the substance in a test tube immersed in a suitable bath.

*Solubility of Sodium Salts.* The following table gives the solubility of two anhydrous salts of sodium which show transition-points.

Solubility in grams of substance in 100 g. water						
		20°	40°	60°	80°	100°
Sodium sulphate <sup>*a</sup> .	4.65	20.4	48.1	45.0	43.2	42.0
Sodium carbonate <sup>*b</sup>	7.0	21.5	46.1	46.0	45.8	45.5

<sup>\*</sup> These two salts have transition-points at 32.5°.  $a = 10$  aq.  $1$  aq.  $b = 10$  aq.  $0$  aq.

## SECTION 2: DENSITY OF SOLIDS

**Units of Density.** The density of any substance is the mass of unit volume, and hence the units of density depend on those of mass and volume, that is, on those of mass and length. In physical chemistry density is usually expressed as grams per cubic centimetre.

The density of water at its point of maximum density, at which the unit of volume is deduced from that of mass is from the definition of the unit of volume obviously 1, but in very accurate work it must be remembered that this unit of density is expressed in grams per millilitre, and that this is not the same as grams per cubic centimetre. The difference involved is, however, very small; it can often be neglected without the introduction of serious error. The figures expressing in the metric system the densities of other substances also express the relative densities of the substances in question relative to that of water as a standard. In other systems of units—for instance, in the pound cubic foot system—this is not so, and the term specific gravity is then employed to denote the density of a substance relative to that of water, from which it follows that the absolute density of a substance is the specific gravity multiplied by the absolute density of water. The specific gravity is also equal to the weight of a volume of a substance divided by the weight of an equal volume of water.

**Measurement of Density.** From the definition, a direct determination of density involves a determination of a mass and a volume. While the former measurement is usually readily accomplished, the latter is often difficult, especially with solids and gases. Solids present difficulties because their shape is fixed, and hence their volume not easy to measure directly, while gases have not a fixed volume for a given mass, but one which varies with temperature and pressure.

The determination of the densities of solids and liquids will be considered here, while that of gases is dealt with in Vol. II, Chapter I\*, S. 6.

**General Considerations.** Before discussing density determinations it is necessary to emphasize the fact that a body has several densities, and that the quantity actually measured is to some extent arbitrary and not fundamental. In a solid body there are, for example, the density possessed by the nuclei of the atoms, or by the electrons, or by the atoms as a whole. All these are constants not readily alterable by any physical means. But the density of a body, as defined above and as usually determined, is a less definite quantity. Salts vary in density when subjected to high uneven pressures, this, presumably, producing a deformation of the crystal lattice. On the other hand, high even pressures have little, if any, effect. Powdering a homogeneous crystalline substance does not greatly, if at all, affect its density. It must be emphasized, however, that it is a matter of difficulty

to obtain really homogeneous crystalline substances owing to the occlusion of foreign matter. usually mother liquor, in internal cavities in the crystals, but that when such crystals are obtained it is theoretically possible to alter the density at a given temperature by physical means, but it appears to be a matter of great difficulty to do so. In metals, however, the internal structure, although based on the crystal lattice, is more complex, and there is a great tendency to form allotropic forms. As a result, the density is rather a variable depending on the previous treatment of the sample under investigation. For example, the density of copper can be altered by several units in the third place by subjection to pressures of the order of 10,000 atm. or to annealing treatment or the like.

Thus Landolt-Börnstein gives for the density of copper figures ranging, according to the treatment the metal has received, from 8.300 to 8.959, while Kahlbaum states that the determination of the density of a metal is a delicate operation which can only be effected with success on large quantities of substance, and the determined value cannot be regarded as a general physical constant, but one applicable only to the sample under investigation.

Before, however, variations in the density of a solid are put down to small changes in its internal structure, all other causes of variation should be investigated. For example, Le Chatelier and Wologdine have shown that the very varying values previously obtained for the density of graphite may be attributed to the presence of impurities in the specimens, and have shown that specimens from different sources may be purified to give almost identical values.

The consistency of the density of ice has been studied by several workers. Differences of the order of 0.1 per cent have been found in the densities of new and old ice and of natural and artificial ice. These, however, are considered to be due to the effect of dissolved air in the ice.

Super-cooled liquids like glass also exhibit considerable changes in density, according to the previous treatment of the sample. With glass the matter is further complicated by the fact that glass is not a substance of absolutely uniform composition nor of stable physical form. For a porous substance like porcelain there may be determined the bulk density (see later), or the density allowing for the pore space. The consistency here obtainable is not very great and the results are of little more than practical interest. Organized substances like cotton fibre may also be submitted to what are called density determinations, but the results obtained are purely empirical; such substances alter in volume very readily. They always adsorb in their pores some of the medium in which they are placed and the quantity adsorbed and hence the final volume of the fibre depends on the viscosity of the medium and on many other external conditions.

Pure liquids, owing to their simpler internal structure, do not present these difficulties. Also they are usually more readily obtained homogeneous. The same applies to gases, but here certain manipulative difficulties have to be overcome.

The importance of density determinations, especially in connexion with liquids, need not be emphasized. Not only are they of use in characterizing a liquid and proving its purity, but they are frequently applied to the accurate determination of volumes (Chap. II, §. 4). Conversely, since the volume of

a liquid is readily measured with fair accuracy, the mass of a given quantity can often be determined in this way.

Apart from its value as a physical constant, in connexion with the determination of molecular volumes, the lattice structure of crystals, &c., the density of a solid is not often employed; it is usually more convenient to measure a given mass by direct weighing, volume relations being seldom considered.

**Non-porous Solids.** By non-porous solids are meant those which if immersed in a liquid do not readily absorb any of the liquid into the interstices between the atoms or molecules. Crystalline substances under the conditions of the investigation, super-cooled liquids, or substances such as metals which may perhaps be regarded as crystalline, are here included.

The most important methods for determining the density of solids are six in number: (1) the volumetric method; (2) by means of the dilatometer; (3) by means of the volumenometer; (4) by means of the pyknometer; (5) by the method of Archimedes; (6) by the flotation method. These methods are all related to one another.

**The Volumetric Method** involves the determination by direct measurement of the volume of a definite weight of the material. Owing to the difficulty of obtaining sufficiently perfect geometrical forms the method is not often employed.

In the other methods the necessary volume determination is replaced by a measurement of the volume of a liquid or gas.

Kahlbaum, Roth and Siedler investigated the possibilities of the method, using an accurately formed cylinder of pure copper, but in spite of all precautions they were not able to obtain results on the one sample closer than 6 units in the second decimal place, an error of nearly 1 per cent.

**The Use of the Dilatometer.** The dilatometer consists of a bulb of suitable material, such as glass, fitted with a capillary tube rising vertically from it. If the bulb is filled with a liquid which also partially fills the capillary tube, then any slight alteration in the volume of the liquid will produce a relatively large change in the level of the liquid in the capillary tube.

The instrument could be employed to determine the actual density of a substance by comparing the changes in level of the meniscus in the capillary tube when known weights of two substances, one of known density, are placed in turn in the bulb. But it is usually applied to follow the variation in volume, and hence in density, of a liquid with temperature. Alternatively, if a liquid the temperature change in volume of which is known be employed, the dilatometer can be used to follow the temperature changes in density of a solid substance. The alteration in the total volume of the liquid and the solid is observed and allowance is made for the change in volume of the liquid and the containing vessel. It is of course essential that the liquid should be without action on the solid.

In practice great difficulty is experienced in maintaining any one temperature sufficiently constant to prevent casual movements of the meniscus. On that account the dilatometer is seldom used at temperatures above 100°, when very great precision is required.

These difficulties, however, can be overcome by making all the observa-



tions differentially with two dilatometers, one containing the working liquid and the solid under test, and the other the liquid alone. Corrections are applied for the fluctuations in temperature by subtracting the readings of the two dilatometers, allowance being made for the unequal quantities of liquid in the bulbs and for the unequal bore of the capillaries. The correction for the expansion of the material of the containing vessel is also eliminated.

**Method of Parker and Lowry.** The following method was employed by Parker and Lowry, in investigating the changes in density which occur in alloys on prolonged heating (Fig. 5 (XII)).

The dilatometers (see Fig. 5 (XII) *b*) were made with bulbs of about 10 ml. capacity. They were cleaned and the filings of metallic alloys under test introduced at A, the capillary B being kept clean by a minute plug of paraffin wax or by passing a wire of suitable diameter down it. When three-quarters full the bulb was sealed at C and filled with air-free liquid by exhausting with a Gaede mercury pump, and then allowing the liquid to enter through the capillary from the apparatus shown (Fig. 5 (XII) *c*). The

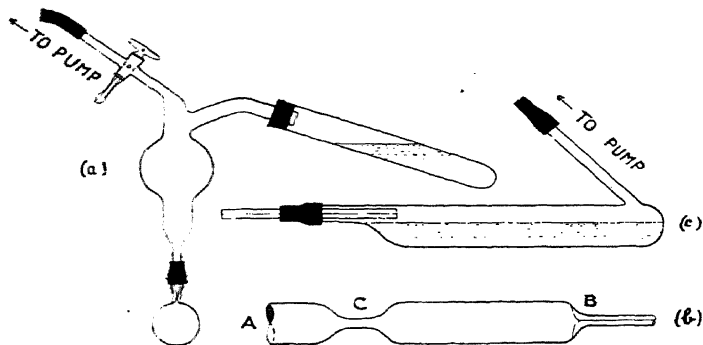


FIG. 5 (XII)

dilatometer when filled is kept at least 12 hours in order that minute air-bubbles amongst the filings may be absorbed; a dilatometer heated immediately almost always commences to liberate gas. Four weighings are needed to determine the weight of metal and of liquid contained in each dilatometer. The density of the metal at ordinary temperature was determined in a small silica pycnometer. The apparatus shown in Fig. 5 (XII) (*a*) being used to fill it with air-free liquid.

The liquid used for filling the dilatometer must, as has been said, be inert so far as the substance under test and the temperatures of the experiments are concerned. It must have a viscosity sufficiently low to pass readily through the capillary tubes of the dilatometer. Paraffin, boiling between 200 and 300°, or xylene can be used. The dilatometers were heated in the vapours of liquids boiling at the temperatures required for the experiments. Aniline, for instance, gave a temperature of about 180°, and so on. Variations in pressure may cause the temperature to vary by some fractions of a degree, but the use of the second dilatometer is equivalent to controlling the temperature to within 0.001°.

The 'thermometer' action in the dilatometers was large, varying from 300 to 500 mm. per degree. As a result, it was necessary to adjust the meniscus at intervals by adding or withdrawing fresh liquid. The corrections were applied by determining from the known volume of the liquids in the dilatometers, the known volume of the metal filings, the coefficient of expansion of metal and liquid, and the dimensions of the dilatometers, the difference in the readings of the two instruments corresponding to a given change in temperature if the density of the metal did not alter except according to its usual coefficient of change with temperature.

Hence, any other change in volume, and so in density, could be detected. The method is extremely accurate and changes in volume of the order of 0.004 per cent are readily detected if not spread over a period of more than 1 day, as otherwise the changes in the temperature of the vapour bath, owing to barometric changes, may become too great to allow for adequate compensation.

*Example.* The following example is from Lowry and Parker's paper :

#### ANNEALING OF ANTIMONY AT 100°

Weight of dilatometer	= 14.366 grams	Antimony = 20.772 grams
Tube removed in sealing	= 1.076 "	(density = 6.641)
Dilatometer and metal	= 34.062 "	Xylene = 4.423 grams
Dilatometer, metal and xylene	= 38.485 "	(density = 0.8)
Bore of capillary, $d$	= 0.1766 mm.	$r^2$ = 0.0000780 cm. <sup>2</sup>
Dummy dilatometer	= 14.344 grams	
Filled with xylene	= 21.711 "	Xylene = 7.367
Bore of capillary, $d$	= 0.1644 mm.	$r^2$ = 0.0000675 cm. <sup>2</sup>

Cubical expansion of antimony : expansion of xylene = 1 : 29

Relative movement of meniscus in two dilatometers for an equal change in temperature :

$$= 7.367 \div (0.8 \times 0.675) : \{4.423 \div 0.8 + 20.772 \div (6.641 \times 29)\} \div 0.780 \\ = 13.64 \text{ (dummy)} : 7.24 \text{ (antimony)}$$

The correction is therefore  $(13.64 - 7.24) \div 13.64 = + 47.0$  per cent of the movement of the dummy

The readings for twenty-seven hours were as follows :

Time	Number of hours	A Antimony	D Dummy	A-D	A-D corrected
10.21	0	{ Dilatometers	hot.		
10.24			practically at 100°.		
10.27	0h5	0 mm.	0 mm.	0 mm.	0 mm.
10.28	0 6	— 3.5	0.0	— 3.5	— 3.5
10.31	0 9	— 8.0	0.0	— 8.0	— 8.0
6.30 p.m.	8 8	— 74.2	— 23.8	— 50.4	— 61.7
10.0 a.m.	23 38	— 99.1	— 28.5	— 70.6	— 84.1
12.30	26 8	— 101.2	— 28.5	— 72.7	— 86.2

Observed fall of meniscus 86.2 mm. Bore of tube 0.1766 mm.

$$\therefore \text{Decrease in volume} = 86.2 \times \frac{\pi}{4} \times (0.1766)^2 \text{ mm.}^3 = 2.11 \text{ mm.}^3$$

$$\text{Initial vol. of antimony} = \frac{20.772}{6.641} = 3128 \text{ mm.}^3$$

$$\text{Percentage change in volume} = \frac{2.11}{3128} = - 0.0675$$

$$\text{Increase of density} = \frac{2.11}{3128} \times 6.641 = + 0.0048$$

The modifications necessary to determine the total change in density of a solid over a range of temperatures will be obvious from the above; the application of the dilatometer to determine the temperature change in density of a liquid will also be clear; a liquid, the temperature change in density of which is known, is placed in the second dilatometer except in the case when great accuracy is not required, one instrument then is used, and corrections applied for the cubical expansion of the vessel.

**Andreæ's Modification of the Dilatometric Method.** Andreæ has modified the dilatometric method so that it can be employed for the determination of the density of solid substances which either lose water of crystallization easily or tend to form crystals occluding mother liquor. A concentrated aqueous solution containing a known amount of the substance under investigation and of water is caused to crystallize in the dilatometer, and the saturated mother liquor, the density and composition of which must be known, is employed as the standard liquid. Thus, all air is excluded from the crystals, and the occluded mother liquor does not affect the result, as it is included with the rest. Comparisons of the results obtained with those given by other methods, notably the flotation method, for stable crystals, readily obtained pure and homogeneous, show that by this method the density of a solid can be obtained with the same degree of accuracy as the density of a gas, say, to within approximately 1 part in 5,000.

**The Volumenometer.** Volumenometers are of two kinds according as they measure directly or indirectly the volume of the solid under examination. The former class includes graduated vessels, e.g. burettes, cylinders, &c., in which the change in volume of a liquid when a solid with which it does not interact is introduced into it, is employed to determine the volume of that solid. This has already been discussed briefly.

The method is not of great accuracy, the error being of the order of 1 per cent, but it is convenient and is often employed in the laboratory.

**Vuilleumier's Method.** A simple, convenient apparatus in which approximate readings may quickly be obtained has been described by Vuilleumier.<sup>1</sup> The apparatus comprises a glass cylinder in which water is filled to a zero mark etched on the side. 100 grams of the solid under investigation are added. The instrument is so graduated that the resulting level of the water gives the required specific gravity immediately. For solids soluble in or attacked by water, or which are not readily wetted by water, petrol, benzene, toluene or the like can be employed.

**Mohr's Method.** A process based on the same principle has been suggested by Mohr. A blackened greased metal pointer is suspended in a beaker and water is poured into the latter until the point and its image on the surface of the liquid coincide. This operation can be performed very accurately. A definite volume of water, greater than the volume to be measured, is removed by means of a pipette, the solid is placed in the beaker and the volume of water required to bring the water level to the suspended point is added from a burette. The difference in volume between the water removed and that added is the volume of the immersed solid. The method gives accurate results with large volumes.

**Second Class of Volumenometer.** The second class of volumeno-

<sup>1</sup> *J. Ind. Eng. Chem.*, 1924, 16, 620.

meter, which was invented by Say, is of advantage when the volume of an irregular body or of a powder is required rapidly with an accuracy of up to 0.1 per cent.

It depends on the determination of the volume of a given enclosure of air by noting the alteration in pressure required to increase or decrease that volume a known amount both before and after the introduction of the solid under examination.

**Use of the Volumenometer.** As there is no contact of liquid and solid this method is the only one available when the density of a solid which, owing to its nature, cannot be immersed in a liquid without decomposition is under investigation.

The method can also be applied to give a density figure for cotton, glass, wool, or the like, provided that they are not so closely packed that the equalization of the air pressures within and without the specimen is hindered.

On the other hand, the volumenometer cannot be employed to measure the volume of solids, such as charcoal, which adsorb gases in quantities related to the applied pressure, or which for any reason evolve gas, water vapour, or the like, in the apparatus. The densities of such solids are best determined by means of the pyknometer. They are first powdered and placed for an extended period in a vacuum in order to remove adsorbed gas.

The densities of liquids with a very low vapour pressure at ordinary temperatures, especially of very viscous liquids, can often be determined conveniently with fair accuracy by means of the volumenometer.

**Regnault's Volumenometer.** The volumenometer devised by Regnault is shown in Fig. 6 (XII). It consists of two tubes mounted in a stand as shown; one of the tubes, *c*, is open, the other, *a*, is connected airtight to a flask, *A*, by means of a screw joint or otherwise, so that the vessel can readily be removed when required. Two three-way taps, *r* and *s*, are provided as shown. There are also two marks, *m* and *p*, on the tube connected to the vessel *A*.

It is first necessary to determine the volume, *v*, of the space between the marks *m* and *p*. This is effected by filling tube *a* from *c* to the mark *m* with pure dry mercury, the tap *s* being left open. Mercury is then run from tube *a* only by means of the tap *r* until the level of the mercury in the tube stands at *p*. The weight of the metal withdrawn gives at once the required volume.

The volume *V* of the flask and the tube *a* to the mark *m* is next estimated. Two methods are available and it is of advantage to apply both and to take the mean of the values found.

In the first method the mercury is adjusted to stand at the level *p* in both tubes with the tap *s* open. The tap is then closed and the barometric pressure *P* under which the air in the flask and the tube *a* to *p*, i.e. in the volume *V* + *v*, stands, is noted. With the tap *s* still closed mercury is poured into *c* until the level of the mercury in the other tube is at *m*. The

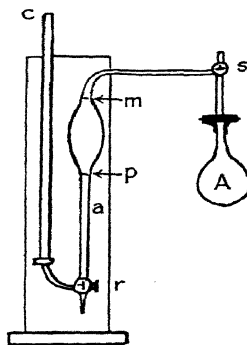


FIG. 6 (XII)

difference,  $\varrho$ , between the levels of the mercury in the two tubes, determined if desired by a cathetometer, plus the atmospheric pressure  $P$ , gives the total pressure of the air in the space  $V$ .

Then, by Boyle's law,

$$P(V + v) = (P + \varrho)V$$

Hence  $V = \frac{Pv}{\varrho}$ , all the quantities concerned being measured in suitable units.

Alternatively, if the mercury is adjusted so that with  $s$  open it stands at the level  $m$  in both tubes, and if after closing  $s$  mercury is withdrawn through  $r$  until the level in the tube  $a$  is at  $p$ , then if the difference in level of the mercury in the two tubes be  $\varrho'$

$$PV = (P - \varrho')(V + v)$$

$$\therefore V = \frac{v(P - \varrho')}{\varrho'}$$

The mean of the two values

$$\frac{1}{2} \left\{ \frac{Pv}{\varrho} + \frac{v(P - \varrho')}{\varrho'} \right\}$$

is then calculated.

The solid, the volume  $x$  of which is under investigation, is introduced in lump or powder form into the flask, and the air volumes  $V - x$  to mark  $m$  and  $V + v - x$  to mark  $p$  determined as before.

If  $P_1$ ,  $\varrho_1$  and  $\varrho_{11}$  are the quantities found corresponding to  $P$ ,  $\varrho$  and  $\varrho'$  respectively, then

$$V - x = \frac{P_1 v}{\varrho_1}$$

and

$$= v \frac{(P_1 - \varrho_{11})}{\varrho_{11}}$$

The mean of the two values of  $x$  is taken.

#### **Lermantow's and other Modifications of Regnault's Apparatus.**

In Lermantow's modification of Regnault's volumenometer the glass flask is replaced by a wide glass tube, and the left glass tube of the apparatus by a cylindrical vessel which is joined to the right tube by a stout piece of rubber tubing. The vessel is raised and lowered by means of a string passing over a pulley and fastened to a small windlass. The removal and addition of mercury is in this way avoided. Teleney and McKeehan fit a barometer tube to a modification of Regnault's apparatus so that all the readings are rendered independent of the barometric pressure. If kept in a constant-temperature enclosure an accuracy of 0.5 per cent is obtained.

**Oberbeck's Volumenometer.** In Oberbeck's instrument two glass tubes fitted with graduated scales are fixed side by side on a horizontal board. They are joined at one end of the board and are thence connected to a mercury reservoir. At the other end each is fitted with a beaker-shaped expansion with a ground edge capable of being hermetically closed. If this is done and the board inclined the mercury falls an equal distance in each tube. But if the body under investigation is introduced into the

expansion of one of the tubes and the board inclined, the mercury in the corresponding tube falls to a less extent. From the data thus obtained the required volume can readily be calculated.

Carman has improved this type of volumenometer, introducing a differential principle so that an accuracy of 1 per cent can be attained when measuring a volume of the order of 2 ml.

**Zehnder's Volumenometer.** The volumenometer designed by Zehnder is specially suitable for density determinations when only a small quantity of the solid is available. The substance is placed in a small stoppered bottle, the internal volume of which is known with accuracy, and the whole is then introduced into the vacuum of a mercury barometer. The air enclosed in the bottle at the time of filling escapes into the space above the mercury, the volume of which is known in terms of the volume of the barometer tube, the material forming the bottle and the substance. This total volume is also known in terms of the original volume of the air and the ratio of its original to its final pressure, which is measured. In this way the volume of the substance is fixed. The chief source of error is the small quantity of air which is adsorbed by the surface of the bottle and by the inner surface of the barometer and tube and which expands when the pressure is diminished. This cannot be avoided; but by performing a blank experiment with the bottle containing air only, or containing a known volume of some standard substance, such as mercury, a correction figure for this can be obtained. Once the apparatus has been calibrated the manipulation is simple and readily performed, and as a means of determining density the method is of great value to chemists and mineralogists. Quantities of the order of 0.1 gram in lump or powder form are sufficient to give results agreeing to within 2 per cent.

The instrument may be modified to give results at any temperature within the range for which mercury is liquid; the bottle and the solid under examination contained in it are heated or cooled to the required temperature before being introduced into the barometer tube.

**Surdo's Volumenometer.** In a new differential type of instrument devised by Surdo, in which an accuracy of 0.1 per cent may be obtained, the fact that halving the pressure on a gas doubles its volume is applied to determine the volume of a solid. The apparatus (see Fig. 7 (XII)) consists of two cups, *a* and *e*, communicating with two vessels, *a'* and *e'*, these being connected through the taps *R*, *S* and *N* to the mercury reservoir *m*. A U-tube which acts as a manometer is also inserted between *a* and *e*, and the connecting tubes between the vessels are marked as *P*, *Q*, *P'*, *Q'*. Then, if the volume *a* equals the volume *a'* equals *V*, and volume *e* equals *e'* equals *V'*

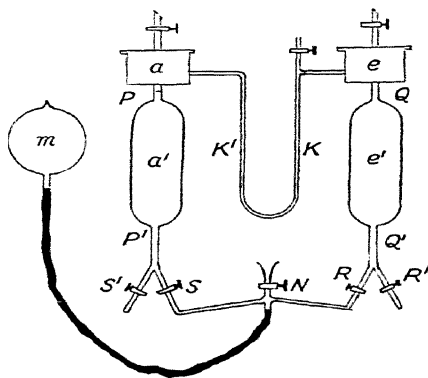


FIG. 7 (XII)

and  $a'$  and  $e'$  are initially filled with mercury up to P and Q, the air above the mercury being at atmospheric pressure H and the level of the liquid in the manometer being equal at KK', on lowering  $m$  until the mercury falls to P' Q' the pressure on the air in the vessel will be reduced to  $H/2$ . If now the original conditions be restored, and there be introduced into  $a$  a body of volume X and the mercury be lowered so that the level in  $e'$  stands at Q', while the level of the manometer is at KK', it is obvious that the volume of air in  $e - e'$  and  $a + a'$  will have been doubled, and that therefore a volume of mercury will have been left in  $a'$  above P' equal to the volume of the body introduced. The volume of this mercury may be determined by having the tube above P' graduated, but it is preferable to weigh it. This may be accomplished by closing tap R and determining the difference in the weights of the quantities of mercury run off through tap R', when the mercury stands at P' and when the weight of mercury it is required to determine is in  $a'$ . Any slight differences in volume between  $a$ ,  $a'$  and  $e$ ,  $e'$ , can readily be ascertained by preliminary experiments with a body of known volume in  $a$ , and these can be eliminated by introducing bodies of the required volumes to render  $a$  equal to  $a'$  and  $e$  equal to  $e'$ . With an apparatus in which V is equal to about 55 ml. it is possible to determine volumes of up to about 45 ml.

**The Use of the Pyknometer.** The pyknometer method is so important that it is necessary to describe it here in some detail. The general precautions to be observed in any method of density determination will here also be included.

The accuracy of the method is great because all measurements of volume are reduced to determinations of mass, i.e. they are thrown back on the fundamental determination of the volume of a given mass of water.

It is possible in this way to obtain the density of a substance correct to one part or even less in a million, when great precautions are taken in weighing, in regulating temperature and in allowing for the effects of humidity. By Lamb and Lee's refinement of the hydrostatic method for liquids (p. 502) it is possible to obtain results correct to one unit in the seventh decimal place. It is questionable, however, whether the amount of impurity in a substance can ever be reduced to such a small amount while the temperature is seldom known to a sufficient degree of accuracy. Temperatures measured with mercury-in-glass thermometers may differ from the International Hydrogen Scale, even when the greatest precautions are taken, by  $0.01^\circ$ . The density of a substance, therefore, at any given temperature may be in error to an amount corresponding to the change in density of the liquid used in the pyknometer for a change in temperature of  $0.01^\circ$ . With water at  $20^\circ$  this error amounts to 1 part in 500,000; with alcohol, acetone, chloroform and the like to 1 part in 100,000. The error is even greater outside the range  $0-100^\circ$ .

With a gas thermometer much greater accuracy can be achieved with care; a temperature at  $0^\circ$  can be determined to  $0.003^\circ$ , at  $60^\circ$  to  $0.006^\circ$ ; but at  $100^\circ$  the limit is only  $0.01^\circ$ . So at  $20^\circ$ , using a gas thermometer, the density of water can be measured as far as temperature is concerned to 1 part in 1,500,000, and of organic liquids to about 1 part in 300,000.

Although the variations in temperature of any liquid which may be

employed to enable the density of a solid to be determined by means of the pyknometer have to be considered, the density of the solid itself is not so sensitive to the influence of temperature. Thus an alteration in temperature of  $0.01^{\circ}$  changes the density of aluminium by only 1 part in 2,000,000.

In general, the pyknometer method, and sometimes the method of Archimedes, is the most suitable for accurate work with solids; the former is especially advantageous when the specimen under test is in powder form.

**General Procedure.** The pyknometer method now to be described involves the weighing of a vessel filled with a suitable liquid and a known weight of a solid under investigation. The vessel is also weighed empty and filled with liquid alone; the density of the latter must be known or determined by weighing the bottle filled with pure water or otherwise. From these weighings the density of the solid can immediately be calculated.

It may be emphasized that in preparing substances for density determinations great care must be taken that they are really pure, as the accuracy of the method is so great that it is sensibly affected by the presence of even small quantities of impurities. Methods, such as fractional distillation, freezing, &c., to be used in purifying the substances will be dictated by their chemical nature and the nature of the impurities known or suspected to be present. No general rules can therefore be laid down, except that it is advisable to consult the literature on previous determinations with the same substance, before deciding on the method of purification to be adopted. Suitable precautions must also be taken to prevent contamination after purification, e.g. finely divided powders adsorb moisture from the air at ordinary temperatures, and this adsorption increases with their state of subdivision.

**The Pyknometer.** The vessel used in the pyknometer method is called a pyknometer or specific gravity bottle; a large number of different forms have been suggested. The most important of these are described here.

A simple form of specific gravity bottle consists of a cylindrical or conical glass vessel provided with a well-fitting ground-glass cap. This gives a con-

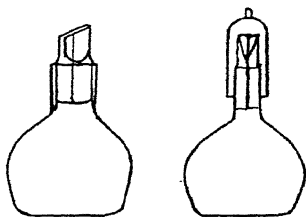


FIG. 8 (XII)



FIG. 9 (XII)

tainer of approximately constant volume. Greater accuracy is attained by the use of bottles of the types shown in Figs. 8 (XII) and 9 (XII), where more accurate adjustment of the volume can be accomplished. The smaller the diameter of the neck the greater the accuracy; in order that substances under examination may readily be introduced the narrow part of the neck is attached to the rest of the bottle by a ground-glass joint. Still greater



accuracy is attained if the exit is reduced to capillary dimensions ; the bottle is completely filled and the capillary stopper introduced ; any surplus over the capacity of the bottle with the stopper in position passes out through the capillary. Very satisfactory results can then be obtained if the measurements are carried out with care. For example, if the bottle has a capacity of about 25 ml., and the capillary is 0.7 mm. in diameter, an error of 1 mm. in the adjustment of the height of the liquid would represent a weight of 0.3 milligram or a temperature of  $0.01^{\circ}$ .

The addition of a ground-on cap to cover the stopper is a necessary precaution when working with volatile liquids. Experiment seems to show that evaporation occurs less by way of the capillary in the stopper than by the ground-joint between the stopper and the neck. When the determinations are made below the room temperature, allowance must be made for the expansion of the liquid as it is heated to the temperature of the balance-case. This is provided for by a small cylindrical cap ground to fit on to the end of the stopper and small enough to go inside the cap. By using the apparatus in the manner to be described later, no difficulty should be experienced in obtaining agreement to the fifth place.

**Liquid Employed.** It has at various times been suggested to employ as the pycnometer liquid substances or solutions of high density in order to increase the accuracy of the results. Among the better known of the liquids which have been suggested are thallium ethylate, solutions of the various borotungstates, and a solution of the double iodide of mercury and potassium. There are, however, objections to the use of most of these heavy liquids, such as the fact that some are too reactive and others too corrosive. On the whole, water is the most suitable, and where its use is precluded, for example, if salts soluble in it are under investigation, xylene is to be recommended. It possesses the advantage that air bubbles are easily removed from it and its volatility is no objection if a capped specific gravity bottle, as described above, is employed.

Carbon tetrachloride has been found satisfactory by Berkeley in determining the densities of crystals (see below).

**Preparation of the Pycnometer Liquid and Filling of Specific Gravity Bottle.** The liquid for density determination is prepared as follows : As much as possible of the dissolved air must be removed, since, apart from any possible effect on the density, when the liquid is put in the warm thermostat there is a tendency for dissolved air to be evolved, and to cling to the glass in the form of very minute bubbles. These are difficult to remove, and, if allowed to remain, a low value for the weight of the liquid is obtained. One method of removing the air is to place a beaker containing the liquid under examination in a vacuum desiccator attached to the water-pump by means of a safety device constructed by fitting to a filter flask a rubber stopper through which passes a vertical tube about 33 inches long, bent down parallel to itself. Mercury is put in the filter-flask, the side-tube is connected to the pump, and the other to the desiccator. The latter is then cut off from the moist air, which is necessary initially if the liquid employed is not water. At the same time, should the water pressure fail, water cannot be sucked back into the desiccator. From 10 to 20 minutes is sufficient to remove the greater portion of the dissolved air. The liquid

is then poured into the weighed S.G. bottle (previously thoroughly cleaned and dried—the usual precautions having been taken) until it is level with the top of the neck (taking care that no air-bubbles are left), and the stopper is inserted.

Alternatively the specific gravity bottle is fitted with a cork or rubber two-hole stopper (for funnel and pump connexions), so that the removal of air from the liquid is accomplished in the bottle. The bottle is evacuated by attachment to a vacuum pump, the liquid slowly admitted and the vacuum maintained for a further 20 minutes.

Kahlbaum, Roth and Siedler have described an elaboration of this apparatus (Fig. 10 (XII) ), consisting of a glass cylinder (A) closed by a ground-in stopper (B), which is itself connected in a similar way to a funnel (C). A three-way tap controls the connexion of B and C via a trap, as above, to a vacuum pump of any suitable kind, e.g. a water or an oil pump. The pyknometer, which may or may not contain the solid according to the stage of the investigation, is placed in the vessel A and into C warm, freshly-boiled distilled liquid, say water, is introduced. The tap is then turned so that C is evacuated and the liquid is boiled under the reduced pressure for some time and is then allowed to remain under the reduced pressure for over an hour. A and B are then evacuated and the water run slowly in from C; any minute air-bubbles may be removed by a small hole. The tap between C and B is then closed and the three-way tap is turned so that B is cut off from the pump and the apparatus dismantled from the latter and allowed to stand in a thermostat overnight, A and B still remaining evacuated. Air is then admitted and the stopper fitted to the pyknometer, as described below.

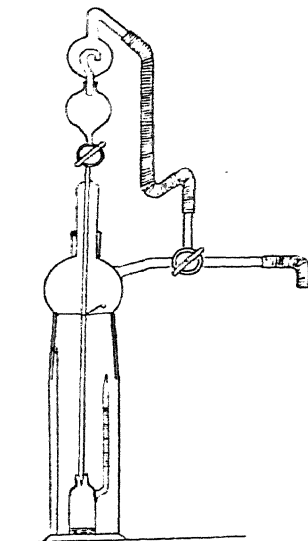


FIG. 10 (XII)

The advantage of this apparatus is that it allows the vacuum to be maintained until temperature adjustment is complete. This prevents any action of air on the liquid or the solid if present.

**Insertion of Stopper and Temperature Adjustment, &c.** The stopper should always be inserted to the same extent each time, advantage being taken of natural or artificial marks to ensure this condition, and undue pressure should be avoided: some workers use exactly the same pressure each time by putting the bottle on a compression balance and pushing the stopper down so that the pointer of the balance moves to a definite mark. For lower temperatures the small cup is placed on the stopper and half filled with water or other liquid under test; this is omitted for temperatures higher than that of the room. The cap, if in use, is put on and the bottle is fastened to a metal holder which keeps it in a vertical position in the thermostat. The holder consists of two parts made to slide on a metal rod

about 8 inches long and held in position by small thumbscrews. The lower part consists of a short support to which are attached three short arms bent upwards and covered with rubber tubing. The upper piece consists of a short support terminating in two rubber-covered arms which encircle the upper part of the bottle below the neck; the holder must not be fastened so tightly as to deform the bottle. The time allowed in the thermostat depends on the accuracy desired; if accuracy to the fifth place is required, the temperature of the liquid must not differ from that of the bath by  $0.01^{\circ}$ , and 1 hour is generally sufficient before the final adjustment is made, but Wade and Merriman recommend 2 hours; to obtain results accurate to the fourth place, 20 minutes to 0.5 hour is quite enough. The cap, including cup if in use, is now removed and dried. The excess of liquid on the top of the stopper is then removed so that the meniscus is just visible on looking through the stopper from the side and the top is quite dry. The bottle is now taken from the bath and quickly dried round the neck, and the cap replaced. The outside of the bottle is wiped with a cloth moistened with alcohol, dried, and the bottle placed in the balance-case, and after half an hour weighed with the usual precautions. The liquid is then poured out and the bottle cleaned.

If a liquid other than water has been employed, and if its density is not known with sufficient accuracy, the bottle is filled with distilled water free from dissolved air and the procedure above repeated. If the highest accuracy is required it is necessary to determine the water content each time the bottle is employed, otherwise slight errors may occur owing to a change in the weight or in the volume of the bottle, due either to a reduction in the size of the stopper by the repeated grinding, or to a slow change in volume similar to that observed in thermometers, or to a slight change in the temperature of the thermostat. Silica pyknometers are sometimes used, and they possess some advantages in certain kinds of work.

The solid under investigation, in lump or powder form as desired, is next placed in the cleaned bottle and the whole accurately weighed as before. The bottle containing the solid is then filled with the liquid which is being used as the standard, and the weight of the bottle, plus the solid, plus the liquid, determined with the precautions described.

To determine the density of the substance under test from the above measurements it is essential that the density of water at the temperature employed should be known accurately. The tables recorded later give the required figures.

Tables of the density of mercury at different temperatures are also included, since it is frequently employed as a standard substance for volume determinations (Chap. II, S. 4). It is not often used in pyknetric work owing to its tendency to distort the specific gravity bottle and to the difficulty of keeping solids below its surface, but it finds applications in other methods of determining density.

**Calculation of Density.** Apart from buoyancy corrections and the like, for which see Chapter II, S. 5, if  $a$  be the weight of the solid under investigation,  $b$  the weight of the vessel filled with the standard liquid the density of which is  $d$ , and if  $c$  be the weight of the vessel filled with liquid and containing the weight  $a$  of the solid, then the weight of the standard

liquid, having a volume equal to that of the solid, is  $b - c - a$ , and the volume of this weight of liquid is  $\frac{b - c - a}{d}$ . Hence the density of the solid, all the weights being expressed in grams, is

$$\frac{a \cdot d}{b - c - a}$$

*Examples.* The following examples will illustrate various refinements which have been employed by different workers to increase the accuracy of the pycnometric method.

**Method of Day and Allen.** To determine the density of feldspars these workers employed the arrangement shown in Fig. 11 (XII). The finely powdered substance under investigation is placed in the specific gravity bottle, and the latter is connected by pressure tubing to a bulb containing distilled water, and the whole evacuated by means of a mercury pump. As soon as most of the air is removed the water is allowed to flow into the bottle, and the whole heated to 40° to ensure the removal of all the air. Any particles carried by the boiling water into the tube, and which are not washed

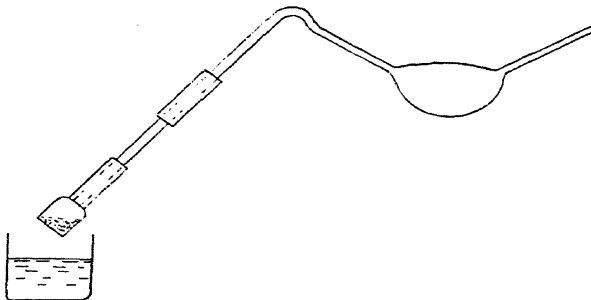


FIG. 11 (XII)

back by the water from the bulb, are afterwards rinsed into a tared dish and their weight determined. The neck of the vessel is also wiped with a filter paper which is afterwards burned in a tared dish and the residue weighed; this obviates any risk of small particles lodging in the ground-glass neck and damaging it. If the powder is very finely divided it is advisable, after filling, to let it stand some hours in the thermostat in order that it may settle completely and an equilibrium condition be attained. With a pycnometer of about 25 ml. capacity, containing about 5–10 grams of solid substance, the errors of the method from all causes should not exceed one unit in the fourth decimal place.

**Method of Johnston and Adams.** Certain difficulties in the use of Day and Allen's pycnometer, when applied to the investigation of the densities of fine powders, are obviated in the improved modification devised by Johnston and Adams. The essential feature of the new form (Fig. 12 (XII)) is the ground joint between the stopper and the bottle. The neck is thickened partly to give increased strength, and partly to minimize heat transfer when the bottle is held between the fingers by the neck. The two

surfaces making up the ground joint should be optically flat, so that when the stopper is pressed on the bottle with a slight rotary motion the bottle may be lifted by the stopper. No lubrication of any kind is employed. Further, in the construction of the pyknometer care is taken that no deep groove exists or any recess from which the excess of water cannot be wiped away.

Pyknometers of this form have the following advantages: The loss in weight by evaporation of the pyknometer liquid is negligible; for water it is of the order of 1 milligram in 24 hours. The pyknometer may therefore be allowed to stand in the balance-case until temperature and moisture equilibrium is attained before it is weighed. No grease or other lubricant is required on this joint, hence this obviates the uncertainty as to the weight of a variable though small amount of such grease. Any small particles of grit or dirt which may accidentally lodge on the ground surfaces can be wiped off quickly and easily. These are the main reasons why the new pyknometer gives more accurate results than the older forms, while its manipulation is not more difficult. With successive fillings and weighings both with water alone, and with the sample and water, the results do not differ by more than 0.2 milligram.

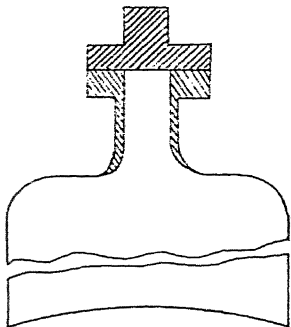


FIG. 12 (XII)

In order to secure these accurate results it is necessary that the determinations be carried out in the following way: The loosely stoppered bottle is immersed in a thermostat, the temperature of which is maintained constant to  $0.01^{\circ}$  (Chap. VI, S. 1) to such a depth that the water level is 2 or 3 mm. below the ground joint, and it is allowed to remain for at least 15 minutes. Enough distilled water at the temperature of the thermostat is then poured into the bottle to fill it to overflowing; less than 1 ml. will be required. The neck of the pyknometer is then held firmly with one hand, while with the other the stopper is pushed on firmly with a sliding and slightly rotary motion. The pressure is still maintained to prevent the occurrence of a slight leak which may be caused by the apparent expansion of the liquid when bottle is removed from the thermostat; this apparent expansion is due to the fact that under these circumstances the bottle cools slightly and contracts, while the temperature of the water remains practically unchanged. The bottle is now wiped dry with a soft cloth. As a precaution, a piece of filter paper is passed around the stopper and the top of the pyknometer, in order to remove any drops of water which may adhere. After standing at least 10 minutes or more in the balance-case the pyknometer is ready to weigh. Great care must be taken not to heat it by hand or otherwise while it is being wiped and removed to the balance-case.

If these directions are followed the stopper will adhere so firmly that the bottle may be held upside down without its falling off. The bottle is then weighed, and the remainder of the fillings and weighings necessary to a determination carried out in a similar manner.

**Determination of Crystal Densities.** The determination of the densities of crystals by the pycnometer method requires special precautions to overcome the possibility of errors caused by air adhering to the crystals, by the hygroscopic nature of some crystals, and by the occlusion of mother liquor by the crystals. An accurate method of obtaining the densities of crystals which do not occlude mother liquor has, however, been worked out by the Earl of Berkeley and may here be described in some detail. The apparatus is two similar conical pycnometers (Fig. 13 (XII)) of Jena glass, of about 7 ml. capacity. They are fitted with carefully ground glass stoppers which also form thermometers standardized and graduated so that they can be read to  $0.01^{\circ}$ . The side capillaries are graduated in millimetres and are calibrated by reading the lengths of weighed mercury threads at different portions of their bores.

The reason for choosing the capacity 7 ml. requires some explanation. The size must be sufficiently great to keep down errors of weighing and manipulation. On the other hand, the greater the capacity of the pycnometer the thicker the walls and, consequently, the longer the time it will take for the larger quantity of liquid to attain a constant temperature when in the balance-case. The size chosen yields a suitable balance of the two opposing effects.

One of the pycnometers is used throughout as a counterpoise. The surface of each pycnometer is similarly treated; if, for instance, one has been filled with carbon tetrachloride and its surface wetted with that liquid, the surface of the other should also be wetted with the same liquid and dried before weighing. The pycnometers, after steaming for 20 minutes, are heated to  $130^{\circ}$  and cooled. This heating and cooling is repeated about fifty times in order to obtain as far as possible a constant state of molecular aggregation of glass.

The capacity of one pycnometer is then determined by filling with distilled water and placing in a small desiccator connected to a Sprengel pump. After vigorous boiling has continued for about half an hour the stopper of the pycnometer is pressed home with a force which is determined by means of a compression balance, and which is always used in subsequent experiments. The capacity of the pycnometer is redetermined at frequent intervals, as slight wear always occurs at the ground-glass stopper.

The pycnometer and its counterpoise are then wiped dry and placed on the pans of the balance, and when the liquid in the capillary has, in consequence of evaporation around the neck, fallen below the highest graduation, the weight is determined, and at the same time the level in the capillary and the temperature of the liquid are noted. Care must be taken that the temperature is fairly constant. The capacity of the pycnometer is then calculated in the usual way, all weighings being corrected for displaced air. In a series of experiments made at temperatures between  $15^{\circ}$  and  $16^{\circ}$  approximately, the greatest difference between any two observations was  $0.00029$  ml., corresponding to an error of  $0.004$  per cent. The mean of the numbers is

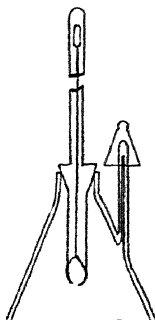


FIG. 13 (XII)

taken as the capacity at the mean temperature, and the capacity at any other temperature is calculated from the known cubical expansion of Jena glass.

The standard liquid employed is carbon tetrachloride, which is carefully purified and filled into the pyknometer in the same way as with water.

Owing to the high coefficient of expansion of this liquid it is essential that the pyknometer thermometer should register the true temperature of the liquid and the glass. A double-walled glass case surrounding the balance-case was in practice found insufficient to secure a steady temperature, and eventually a zinc tank filled with water and placed over and around the three sides of the balance was employed, while the heat of the observer was cut off on the fourth side by a glass trough filled with water. The pyknometer thermometer then indicated a constant temperature, not changing by more than  $0.01^{\circ}$  in 15 minutes after 1.5 hours in the balance-case.

The density of the carbon tetrachloride employed was first carefully determined by the pyknometer method. To determine the density of the crystals the pyknometer, containing a known weight of salt, is placed in a bell-jar connected to a bulb containing carbon tetrachloride. The liquid is caused to boil by exhausting air through the apparatus and after 45 minutes the bulb is tilted so that liquid flows into the pyknometer, which after filling is weighed as described.

The above method proved successful with crystals which adsorbed air on their surfaces; it could also be adapted to the case of hygroscopic crystals by first drying the crystals placed in the pyknometer in a current of air. But it was not successful with crystals which occlude mother liquor; the densities of such crystals must be determined by the methods given previously.

**The Method of Archimedes.** This method involves the weighing of a body in two media of known density. From the difference in the weights obtained the density of the body can at once be calculated. The two media usually employed are air and water, but in place of weighing in air the operation can be carried out in a vacuum, while water can be replaced by any other suitable liquid. To weigh the body in the liquid it is necessary to suspend it in the latter, and it is here that the most serious source of error is encountered owing to the action on the suspending wire of surface tension at the upper boundary of the liquid. These and other errors can, however, be eliminated, and for the determination of the densities of metals and of other materials which may be put in compact form the method is probably the most accurate. With suitable precautions the error can be reduced to at most 1 part in 10,000. A similar accurate method can also be applied to liquids.

When water is employed as the liquid to be displaced it must be boiled and cooled *in vacuo*, otherwise the determinations are vitiated by the presence of air bubbles. The surface-tension effect can be made very small by using an extremely fine platinum wire previously coated with platinum black. In this way Kahlbaum was able to obtain concordant measurements on the same piece of metal.

**Method of Egerton and Lee.** Egerton and Lee<sup>1</sup> have found, however, that with certain mobile organic liquids the damping is very little less than

<sup>1</sup> *Proc. Roy. Soc.*, 1923, 103 A, 487.

in air, and that accurate weighings can be made by the method of swings. They make the suspension as light as possible by employing a very fine aluminium wire weighing less than a milligram, so that the weight of the part of the wire immersed is only a very small fraction of a milligram; even then there is a considerable surface-tension correction which has to be determined carefully. By applying such corrections they have been able to obtain determinations agreeing to within 1 part in 10,000 on samples of the order of 1 gram; previous investigators have, for the most part, used not less than 5 grams. We will describe their method in detail, as it represents the most accurate application of the principle of Archimedes yet achieved.

The sample of metal under investigation (lead) was cast in the form of a small cylinder and suspended by a loop of fine aluminium wire, 0.0015 inch diameter, within a vessel 7 cm. diameter filled with the liquid employed (ethylene dibromide) to a definite mark. A multiple thermocouple was used to measure the temperature of the sample immediately before and after the swings of the balance were observed, and as the couple was frequently and carefully standardized the temperature could be measured to  $0.002^{\circ}$ . At the end of the set of weighings in a liquid, the suspension was cut at the exact height of the immersion and the weights of the two parts of the wire found separately and also the weight of the sample. In comparative measurements, using the same suspension where absolute densities are not required, it may often be unnecessary to cut the wire.

The weight of the part immersed in ethylene dibromide amounted only to 0.02 milligram, so that with a piece of metal weighing 10 grams this weight was negligible.

**Liquid Employed.** For accuracy the liquid should be as dense and as mobile as possible, and non-volatile; it should also dissolve as little air or water as possible, and bubbles of air should be difficult to form. Ethylene dibromide was found sufficiently satisfactory in most of these respects by Egerton and Lee; carbon tetrachloride was also good but rather too volatile.

**Density Formulae.** The approximate value of the density of the solid employed is given by the expression

$$\frac{\text{Wt. of solid in air}}{\text{Wt. of solid in air} - \text{Wt. of solid in water}}$$

This value requires correction for the buoyancy of air, and for the deviation from standard value of the density of water at the temperature of weighing.

It also requires modification if a liquid other than water is used. Following is the calculation of an accurate formula; it is assumed that the temperature and pressure of the air are constant throughout the two weighings, since this is not difficult to achieve experimentally and simplifies the calculation.

If  $\rho$  is the density of the substance

$\rho'$  the density of the liquid

$\sigma$  is the density of the air at the temperature and pressure of the observations

$M_1$  is the mass of the weight *in vacuo* for the substance alone in air



$M_2$  is the mass of the weight *in vacuo* for the substance alone in the liquid  
(after allowing for suspension)

$m$  is the weight (at air standard) of the substance weighed in air

$W$  is the apparent loss of weight of the substance in the liquid, the weights  
being at air standard

$l$  is the weight of air displaced by the substance, or by an equal volume of  
liquid

then

$$\sigma = \frac{m + l}{W + l} \varrho' = \frac{m}{W} (\varrho' - \sigma) \quad \sigma = \frac{M_1}{M_1 - M_2} (\varrho' - \sigma)$$

and it also follows that

$$\sigma = \frac{M_1(1 + \sigma/\varrho)\varrho'}{M_1(1 + \sigma/P - M_2)}$$

where  $\sigma/\varrho$  is small, so that any of these formulae may be used to determine the density of the substance.

It is often most convenient to find  $X = W + l$ , i.e. the weight of an equal volume of the liquid corrected to vacuum standard, and then reduce the observations to a common standard by means of the formula

$$X_t = X_{t'} \cdot \frac{\varrho'_{t'}}{\varrho'_t} \{1 + \alpha(t - t')\}$$

where  $\alpha$  is the coefficient of cubical expansion of the substance.

**Surface-tension Correction.** If the surface-tension correction is not made or the effect eliminated as described above, erroneous results will be obtained, especially with small samples. In spite of the fine suspension, the density was found in the series of experiments at present being described to vary with the weight of the sample, and also with the diameter of the wire employed, as was only to be expected. The correction is obtained as follows:

If  $\eta$  be the constant surface-tension factor for a given wire and liquid we have

$$\varrho'_{(\text{corr.})} = \frac{m_t + l_t}{W_t + l_t + \eta_t} \varrho'_t$$

so that if the weight of the sample is large enough the correction term becomes negligible.

Egerton and Lee employed the above relation in the form

$$\varrho'^{(\text{false})} = \varrho'^{(\text{corr.})} (1 + \eta/x)$$

This formula shows how the apparent density ( $\varrho'^{(\text{false})}$ ) varies with the weight of the liquid displaced,  $\eta$  being practically constant. The above formulae have been tested by experiment with samples of lead of from 1 to 12 grams in weight, cut from a single vacuum casting. Using ethylene dibromide as the liquid and inserting  $\eta = 0.00061$  into the formula,  $\varrho'^{(\text{corr.})}$  was found to agree with a probable error of 1 part in 100,000. Employing  $20^\circ$  as the standard temperature at which to compare the densities, and combining the various corrections, it follows:

$$\varrho'^{20^\circ}_{(\text{corr.})} = \varrho'^{(\text{false})} - \varrho'^{20^\circ}/\varrho'_t \cdot \frac{x_t}{[x_t \cdot \varrho'^{20^\circ}/\varrho'_t \cdot (1 + \alpha(20^\circ - t) + \eta_{20})]}$$

It is, of course, necessary to apply air corrections for the weights and samples. The weighings should be carried out as described, the zero of the balance and the balance sensitiveness being determined before and after every weighing. The weights must also be standardized and the rider arm of the balance calibrated.

**Application to Powders.** The method is not often applied to powdered substances, but fairly accurate values can be obtained by placing the powder in a suitable container which is itself suspended from the wire. The cage is regarded as part of the suspension wire and weighed first with and then without the specimen.

**Solids Lighter than Liquid Employed.** When the solid floats on the liquid chosen, a sinker is attached. This, like the cage used with powders, is regarded as part of the suspension wire.

**Dupré's Application of the Principle of Archimedes.** Dupré's apparatus, by means of which a large number of densities can be determined rapidly and accurately, is shown in Fig. 14 (XII). It consists of a float, which is formed of two wooden pans joined by three steel wires. The upper pan carries beneath it an inverted cup and a pointer. The float is arranged so that the cup is immersed in mercury in a beaker, and sufficient weights are placed in the lower scale pan to bring the pointer just into contact with the surface of the mercury. The substance under investigation in lump form is next placed on the lower pan, and the weights which with it bring the pointer into contact with the mercury surface determined. These two measurements give at once the weight of the body in air. It is next placed under the inverted cup attached to the top float and its apparent weight immersed in mercury similarly obtained. The density can at once be calculated from the known density of mercury, the high value of which enhances the accuracy of the method; it is not, however, sufficiently accurate to necessitate the application of air-buoyancy corrections or the like.

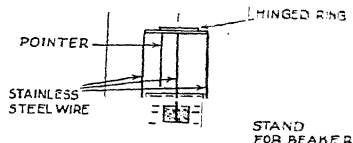


FIG. 14 (XII)

By fitting the float with a rubber cap, which can be hermetically fastened to the beaker, all air can be removed from the substance under test before immersing it in the mercury. To use the apparatus with a substance in powder form a small open vessel of known mass and density is employed to contain the powder.

The so-called float-temperature method has been employed by Briscoe and his collaborators<sup>1</sup> to determine the deuterium content of small amounts of water. With 150 ml. samples an accuracy of 1 part in 5,000,000 is claimed for the method of flotation.

<sup>1</sup> *J. Chem. Soc.*, 1934, 145, 1210. See also Richards and Shipley, *J. Amer. Chem. Soc.*, 1912, 34, 599; 1914, 36-1; Richards and Harris, *ibid.*, 1916, 38, 1000.

In discussing small differences of density of the order here involved the ordinary unit is inconveniently large. They therefore adopt the device current in microchemistry and call one millionth of the ordinary unit a *gamma* of density:  $0.000,001\Delta d = 1\gamma d$ . The error of their comparisons is  $2 \times 10^{-7}$  gram ml. or  $0.2\gamma d$ , and this permits the detection of a change of about 2 parts per million in the isotopic ratio of hydrogen.

The method consists in observing directly the temperature at which a float completely immersed in the liquid remains exactly suspended, neither rising nor falling. The coefficient of expansion of the liquid being known, a second similar observation with the same float in the standard liquid gives a direct comparison of the densities. The chief requirement is a float of convenient density, unchanging in size and weight and insoluble in the liquid. The other requirements are insoluble containing vessels for the liquid, accurate thermometry and an accurate thermostat adjustable over a range of several degrees. Fused silica is the ideal material for the float because of its small thermal expansion, great elasticity, mechanical strength, permanence and insolubility. Briscoe employed a slim cylindrical float about 75 mm. long  $\times$  4 mm. in diameter, and had a ring at the top so that it could be conveniently handled by means of a glass hook.

The design of the float is of some importance. A slim cylindrical float is preferable, since its movement responds more rapidly and certainly to small differences in the density of the liquid. The tube was drawn from 4-mm. silica and showed no change in density in 5 months. Richards and Shipley<sup>1</sup> had previously advocated a float, made in a fish-like form.

**The Flotation Vessels.** The containers used for the flotation temperature determination were large test-tubes of the form shown in Fig. 15 (XII) provided with ground-in stoppers which served as spray traps during the outgassing of the liquid by boiling in a vacuum. They were made of Pyrex glass. After preliminary cleansing with hot chromic-nitric acid, the tubes were extracted with nitric acid at 100° for 24 hours and then thoroughly washed and steamed. The thermometers had a range of 12–22° and were graduated in 0.02°, these graduations being so spaced that it was possible with the aid of suitable magnifiers to estimate temperature within  $\pm 0.001^\circ$ . A thermostat of 20 litres capacity was used and was accurate to  $\pm 0.001^\circ$ . The containing vessel containing 150 ml. of the sample introduced with many precautions, was placed in the vessel. The float was observed with a cathetometer telescope having a Leitz micrometer eye-piece graduated in 0.001 mm.



FIG. 15 (XII)

An all-glass apparatus with standard ground joints for the measurement of the density of glasses at normal temperature by flotation has been described by Seddon.<sup>2</sup> Values for the density of glass in gram/ml. at 25° may be repeated to within  $\pm 0.0001$  gram/ml. A list of immersion liquids suitable for glasses of various types is given in the original paper.

**Densities of Solids at High Temperatures.** Day and Sosman have

<sup>1</sup> *Loc. cit.*, 1912.

<sup>2</sup> *J. Sci. Inst.*, 1937, 14, 376.

used an apparatus similar in principle to Dupré's to determine the densities of silicates at elevated temperatures. The beaker of mercury is replaced by a bath of molten tin, the float is made of Acheson graphite, and the whole arranged so that it can be heated in an electric furnace.

**Nicholson's Hydrometer.** Nicholson's hydrometer is exactly similar in principle to the apparatus described above. Weights are added to the upper pan until it floats in water to a fixed mark on its stem, without the specimen, with the specimen in the upper pan, and finally with the specimen in the lower pan. This method is not susceptible of very great accuracy.

**The Flotation Method.** This method is useful for the determination of the densities of small crystals, or for waxes or hard fats.

The method depends on the principle that a solid will only just float in a liquid of the same density as itself. The range of densities covered by the method depends on the densities of the liquids available. Methylene iodide is particularly suitable as a standard liquid. It has an approximate density of 3.3, and by dilution with benzene or its homologues this may be decreased to 0.9. For substances which are attacked by these liquids an aqueous solution of potassium mercuric iodide can be employed.

The method is very sensitive provided the temperature of the liquid is accurately controlled. The chief error arises from the adsorption at the surface of the specimen; the adsorbed layer may consist of a thin air film, or it may be composed of the liquid medium or of one of its constituents. As a result of this, because the smaller particles have a relatively larger surface area, if the density of a powder is investigated, some particles will be found to sink and some to rise. In spite of its sensitiveness the errors involved in the method are relatively large owing to the small size of the fragments for which it is usually employed.

It was originally designed for the determination of the densities of crystals of salts soluble in water. Such crystals are seldom free from occluded mother liquor, and it is difficult to separate those crystals which are pure and homogeneous. Retgers accomplished this, however, by placing a powdered crystalline salt in a liquid of its own density; the heaviest crystals which just sink are pure; those containing even traces of mother liquor float on the surface. Further, the density of the mixed liquid employed gives at once that of the pure crystals.

The densities of a liquid, available only in very small quantities, can also be obtained by this method, using as flotation media liquids with which the specimen under test is completely immiscible, e.g. for oils, suitable aqueous salt solutions.

**Apparatus Employed.** A small dropping funnel of about 20 ml. capacity is half filled with methylene iodide, some crystals are then added which float on the surface of the liquid, assuming that they possess a lesser density. Benzene is introduced slowly from another funnel, the whole being shaken after each addition. In time it will be noted that the crystals only rise slowly to the surface after shaking. The benzene is then added drop by drop with vigorous shaking, care being taken not to warm the liquid in the funnel by the heat of the hand. When the crystals float in any portion of the liquid without rising or falling the temperature and composition of the

mixed liquid are noted and its density at that temperature determined by any suitable method.

**Substances of High Density.** If the substance sinks in the densest liquid available, a crystal is attached to a glass float made of a glass rod bent into a horse-shoe form, so that the crystal can be inserted and held firm between the extremities.

If  $W$  is the weight of the float

$W_1$  " " " " crystal

$d$  the density of the float

$D$  " " " " and crystal combined (i.e. the liquid in which they just sink)

then  $\rho$  the density of the salt is given by the expression

$$\rho = \frac{D}{\{1 - W/W_1(D/d - 1)\}}$$

The best results are obtained when  $W$  is made as small and  $W_1$  as large as possible.

The method could similarly be applied to very light substances by the employment of a sinker, but this is seldom or never necessary.

**Andrae's Modification.** Andrae greatly improved the accuracy of the method by placing a small homogeneous crystal of the substance together with a liquid mixture of approximately the same density in a graduated dilatometer which is placed in a thermostat, the temperature of which is altered until the crystal just floats. From the weight and known volume of the dilatometer, the density of the liquid can be determined very accurately, while by obtaining data at different temperatures the coefficient of expansion of the crystal can be obtained.

**Density of Porous Solids.** The density of a porous body, e.g. coke or ceramic material, is usually taken to mean the average density of the cellular and solid mass contained in the specimen; if this apparent density is required the body may be coated with a thin film of wax and any suitable method applied.

Another method is to weigh the body in air ( $W_1$ ), then in water ( $W_2$ ), and finally, after wiping with a moist cloth, in air again ( $W_3$ ). Then the weight of water adsorbed in the pores is equal to ( $W_3 - W_1$ ), and the loss in weight of the body in water if no water had entered the pores is  $W_1 - W_2 + W_3 - W_1$ , i.e.  $W_3 - W_2$ , hence the apparent density

$$W_1$$

Some writers recommend boiling for some hours with water under reduced pressure in order to fill as much of the pores as possible with water before weighing in that liquid; the amount of water adsorbed is then determined, but this does not appear to be necessary.

A figure nearer to that for the density of the solid material can be obtained by reducing the substance to a fine powder and boiling in liquid for some time before using the pyknometer or other methods. Even then a number of the cells do not get penetrated by the liquid.

DENSITY OF WATER, FREE FROM AIR, FROM 0°-41° IN GRAMS PER  
MILLILITRE

°	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Mean differ- ences
0	0.9998681	8747	8812	8875	8936	8996	9053	9109	9163	9216	+ 59
1	9267	9315	9363	9408	9452	9494	9534	9573	9610	9645	+ 41
2	9679	9711	9741	9769	9796	9821	9844	9866	9887	9905	+ 24
3	9922	9937	9951	9962	9973	9981	9988	9994	9998	0000*	+ 8
4	1.0000000	9999*	9996*	9992*	9986*	9979*	9970*	9960*	9947*	9934*	- 8
5	0.9999919	9902	9884	9864	9842	9819	9795	9769	9742	9713	- 24
6	9682	9650	9617	9582	9545	9507	9468	9427	9385	9341	- 39
7	9296	9249	9201	9151	9100	9048	8994	8938	8881	8823	- 53
8	8764	8703	8641	8577	8512	8445	8377	8308	8237	8165	- 67
9	8091	8017	7940	7863	7784	7704	7622	7539	7455	7369	- 81
10	7282	7194	7105	7014	6921	6826	6729	6632	6533	6432	- 95
11	6331	6228	6124	6020	5913	5805	5696	5586	5474	5362	- 108
12	5248	5132	5016	4898	4780	4660	4538	4415	4291	4166	- 121
13	4040	3912	3784	3654	3523	3391	3257	3122	2986	2850	- 133
14	2712	2572	2431	2289	2147	2003	1858	1711	1564	1416	- 145
15	1266	1114	0962	0809	0655	0499	0343	0185	0026	9865*	- 156
16	0.9989705	9542	9378	9214	9048	8881	8713	8544	8373	8202	- 168
17	8029	7856	7681	7505	7328	7150	6971	6791	6610	6427	- 178
18	6244	6058	5873	5686	5498	5309	5119	4927	4735	4541	- 190
19	4347	4152	3955	3757	3558	3358	3158	2955	2752	2549	- 200
20	2343	2137	1930	1722	1511	1301	1090	0878	0663	0449	- 211
21	0233	0016	9799*	9580*	9359*	9139*	8917*	8694*	8470*	8245*	- 221
22	0.9978019	7792	7564	7335	7104	6873	6641	6408	6173	5938	- 232
23	5702	5466	5227	4988	4747	4506	4264	4021	3777	3531	- 242
24	3286	3039	2790	2541	2291	2040	1788	1535	1280	1026	- 252
25	0770	0513	0255	9997*	9736*	9476*	9214*	8951*	8688*	8423*	- 261
26	0.9968158	7892	7624	7356	7087	6817	6545	6273	6000	5726	- 271
27	5451	5176	4898	4620	4342	4062	3782	3500	3218	2935	- 280
28	2652	2366	2080	1793	1505	1217	0928	0637	0346	0053	- 289
29	0.9959761	9466	9171	8876	8579	8282	7983	7684	7383	7083	- 298
30	6780	6478	6174	5869	5564	5258	4950	4642	4334	4024	- 307
31	3714	3401	3089	2776	2462	2147	1832	1515	1198	0880	- 315
32	0561	0241	9920*	9599*	9276*	8954*	8630*	8304*	7979*	7653*	- 324
33	0.9947325	6997	6668	6338	6007	5676	5345	5011	4678	4343	- 332
34	4007	3671	3335	2997	2659	2318	1978	1638	1296	0953	- 340
35	0610	0267	9922*	9516*	9230*	8883*	8534*	8186*	7837*	7486*	- 347
36	0.9937136	6784	6432	6078	5725	5369	5014	4658	4301	3943	- 355
37	3585	3226	2866	2505	2144	1782	1419	1055	0691	0326	- 362
38	0.9929960	5993	5627	5259	4890	4520	4150	3780	3410	3040	- 370
39	6263	5890	5516	5140	4765	4389	4019	3643	3255	2876	- 377
40	2497	2116	1734	1352	0971	0587	0203	9818*	9433*	9047*	- 384
41	0.9918661	—	—	—	—	—	—	—	—	—	—

The asterisks in the table imply that the first three figures are those of the line below. The temperatures are on the International Centigrade Hydrogen Scale.

The above table is from the observations of Chappuis, which agree with those of Thiesen, Scheel and Diesselhorst to within a few units in the sixth decimal place; the differences are mostly at the higher temperatures.

DENSITY OF WATER FROM 40–100° IN GRAMS PER MILLILITRE  
Temperatures on the International Centigrade Hydrogen Scale :

40	0.992244	1858	1466	1066	0658	0244	9823*	9395*	8960*	8518*
50	988070	7615	7154	6686	6212	5731	5245	4752	4253	3748
60	983237	2720	2197	1688	1134	0594	0047	9496*	8939*	8376*
70	977808	7234	6655	6071	5481	4886	4285	3679	3068	2452
80	971831	1205	0573	9937*	9295*	8649*	7998*	7341*	6680*	6014*
90	965343	4668	3987	3302	2612	1918	1218	0514	9806*	9093*
100	958375	7653	6926	—	—	—	—	—	—	—

DENSITY OF WATER BETWEEN 100° AND 320°

The table gives the mean of the values of Ramsay and Young, Waterston and Hirn.

	100	120	140	160	180	200	220	240	260	280	300	320
Density	0.9584	9434	9264	9075	8866	8628	0.837	0.809	0.779	0.75	0.70	

DENSITY OF WATER SUPERCOOLED BELOW 0°

— 5                      — 10

Density . . . 0.99987      0.99930      0.99815

Landolt-Börnstein gives also tables for the density of water at various pressures.

DIFFERENCE BETWEEN THE DENSITY OF WATER CONTAINING AIR ( $d'$ ) AND  
FREE FROM AIR ( $d$ )

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	19	20	
10 <sup>7</sup> ( $d' - d$ )	25	27	29	31	32	33	33	34	34	33	32	31	29	27	25	22	19	16	12	8	4

According to Chappuis between 5° and 8° 10<sup>7</sup>( $d' - d$ ) = — 30.

### SECTION 3: DENSITY OF LIQUIDS

The density of a liquid is, on the whole, more simply determined than that of a solid. Three main methods are available: (1) Pyknometric methods; (2) Displacement and flotation methods; and (3) Hare's method and its modifications.

**Pyknometric Methods.** The method will be clear from what has been said on the use of the pyknometer to determine the densities of solids.

As with the latter, a great variety of pyknometers is available, which differ from those previously described in that they are not provided with wide openings, since only liquids have to be introduced into them. It will of course be obvious that many types of pyknometer used for a solid can also be employed to determine a liquid density.

**Types of Pyknometers.** The simple specific gravity bottle with drilled stopper and cap, is extensively used.

Sprengel's pyknometer and its many modifications are employed where more accurate results or more rapid workings are required (Fig. 16 (XII)); e.g. a simple self-filling pyknometer has been devised by Hennion.<sup>1</sup>

Perkin's modification consists of a U-tube holding from 2-10 ml. and fitted at each end with capped capillaries, which are bent outwards at right angles to each other.

One capillary limb is widened into a bulb to enable the instrument to be weighed full of liquid at a temperature above that at which it was filled. This is accomplished by drawing the liquid into the dried and weighed pyknometer through the limb *b* until it half fills the bulb on the limb *a*. The apparatus is then maintained at the required temperature and the meniscus of the liquid in *a* adjusted to a mark on it below the bulb. To do this the whole is tilted until *b* is horizontal, when, as the limbs are bent at right angles to each other, *a* will be found to be vertical. A piece of filter paper is applied



FIG. 16 (XII)

to the end of *b* until the liquid sinks to the required mark. The U-tube is then brought to the vertical position, and the glass caps placed in position. The weighings are carried out in the usual way, there being determined the weight of the pyknometer empty, full of pure water, and filled with the liquid under test. The density is calculated as described later.

<sup>1</sup> *Ind. Eng. Chem., Anal. Ed.*, 1937, 29, 479.



**Wade and Merriman's Modification of Gay-Lussac's Pyknometer.**

This (Fig. 17 (XII)) consists of a small flat-bottomed flask with a capillary neck expanding at the top to a small cup which is closed by a rubber stopper; there is also a special filling apparatus. With a 25 ml. pyknometer having a neck of 0.7 mm. internal diameter, an error in setting of 0.1 mm. corresponds to an error of about one in the sixth place. The india-rubber stopper is used with the idea of preventing the small vapour leak which occurs with ground-glass joints; but rubber absorbs some vapours, e.g. chloroform, so readily, and is altogether so difficult a substance to weigh exactly that it is better to use a well ground-in glass stopper instead. The type of losses to be expected by this leak are shown by the following figures:

	Bousfield pyknometer 70 ml.	S.G. bottle with cap 50 ml.
Weight after 45 min. in balance-case .	114.3722 grams	66.6592 grams
Weight after 90 min. in balance-case .	114.3643 "	66.6588 "
Loss in 45 min. . . . .	0.0079 "	.0004 "
Temp. of balance-case = 25°. Ether was the liquid used.		

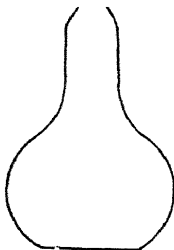


FIG. 17 (XII)

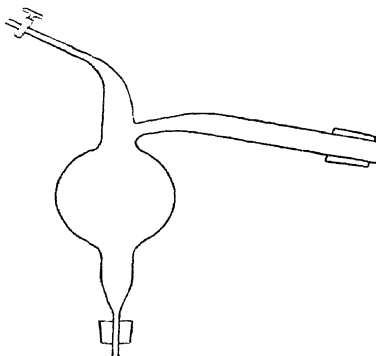


FIG. 18 (XII)

In this method the stopper can always be inserted to exactly the same extent in the bottle. It can also be filled easily without letting the liquid come in contact with moist air. The filling apparatus (Fig. 18 (XII)) consists of a glass bulb to which are connected three tubes: one of these passes from the bottom down through a rubber stopper to the pyknometer; the other two project from the top of the bulb, one vertically, to which is attached a three-way tap so that connexion can be made to the pump or to a tube for admitting dry air, the other projecting horizontally and then bending downwards to the round-bottomed flask containing the liquid.

Filling is carried out by first exhausting and then tilting the apparatus so that the liquid runs towards the pycnometer; on admitting dry air some liquid is forced into the pycnometer and by repeating the process it can be completely filled. A small air-bubble is introduced with the aid of a drawn-out tube, the pycnometer is emptied, and is then attached in an inverted position to the filling apparatus. By repeating the exhaustion and filling with dry air, the liquid can be returned to the flask without coming into contact with moist air. The repeated admission of dry air and its subsequent exhaustion is a rapid and efficient method of drying the pycnometer. The adjustment in the thermostat is made by removing with filter paper the excess of liquid in the cup, and then the liquid in the capillary down to the mark, by means of a rolled-up piece of filter paper, or a finely drawn-out tube in which the liquid rises by capillarity. A lens can be used to view the position of the meniscus. Air is blown into the cup to remove vapour and the stopper is put in place.

**Browne's Pycnometer.** A combined specific gravity bottle and dilatometer has been described by Browne for determining the small changes of volume which occur when sugar solutions undergo inversion or when sugar solutions are mixed. The apparatus consists of a narrow tubular body holding 30 ml. connected at the bottom with a capped graduated capillary tube and contracting at the top to a small opening. The latter is slightly funnel-shaped and is ground on its inner surface so as to receive a thermometer which is also ground so as to fit tightly on insertion. The displacement of the thermometer is about 7 ml., and this leaves a capacity of 23 ml. for the instrument when stoppered.

The scale upon which the changes of volume are measured is graduated so that one division equals 0.001 ml., and by means of a magnifying glass reading can be made to 0.0001 ml. The apparatus can be used in the same manner as an ordinary pycnometer, and as a dilatometer it can be employed to follow the changes in volume or density of a liquid with temperature.

The Bousfield pycnometer consists of a U-tube holding from 70 to 250 ml. (Fig. 19 (XII)). Each arm of the U terminates in a capillary neck expanding to a cup at the top. The ends of the U are connected by a piece of solid glass which serves to attach a platinum wire to hang up the apparatus in the balance-case or the thermostat. A piece of lead hung on the lower part of the U keeps it vertical, and so assists in the adjustment. Sometimes the solid piece of glass is replaced by a narrow tube with the idea of facilitating the filling of the apparatus; there is, however, little difficulty in filling by suitably tilting the apparatus, while the tube acts as a trap for bubbles. Glass stoppers are provided and ground-in glass tubes are sometimes used to assist in filling by suction. This apparatus has the advantage of having a large volume and a relatively large surface so that thermal equilibrium is rapidly attained; it is also easy to clean. It has the disadvantage of having

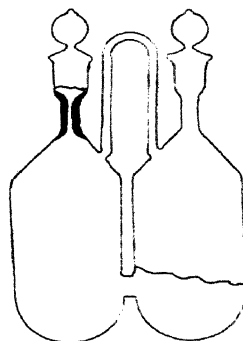


FIG. 19 (XII)

two ground-glass stoppers with the increased chance of leakage, and of the larger air-space in the cups which may lead to some uncertainty in the vacuum correction. Perhaps it would be worth while to use two sets of stoppers, shallow ones leaving a large air-space in the cups for use in the thermostat, and deeper ones almost filling the cups for use during the weighing.

**Pyknometric Formulae.** Following is the complete formula for determining the density of a liquid from observations taken with a pyknometer :

Let  $W_P$  = observed weight in grams of pyknometer in air of density  $\sigma_1$  gram/ml.

$W_W$  = observed weight in grams of pyknometer filled with water of temperature  $t_W$  in air of density  $\sigma_2$  gram/ml.

$W_L$  = observed weight in grams of pyknometer filled with liquid of temperature  $t_L$  in air of density  $\sigma_3$  gram/ml.

$\Delta$  = density of weights employed in gram/ml.

$G$  = density of glass in gram/ml.

$d_W$  = density of water at  $t_W$  in gram/ml.

$d_L$  = density of liquid at  $t_L$  in gram/ml.

$\alpha$  = coefficient of cubical expansion of glass in ml. per ml. per ° C.

$M_P$  = mass *in vacuo* of pyknometer

$M_W$  = mass *in vacuo* of water required to fill pyknometer at temperature  $t_W$

$M_L$  = mass *in vacuo* of liquid required to fill pyknometer at temperature  $t_L$

Then, considering the weighing of the pyknometer alone, filled with water and filled with liquid, we have :

$$W_P \left( 1 - \frac{\sigma_1}{\Delta} \right) = M_P \left( 1 - \frac{\sigma_1}{G} \right)$$

$$W_W \left( 1 - \frac{\sigma_2}{\Delta} \right) = M_W \left( 1 - \frac{\sigma_2}{d_W} \right) + M_P \left( 1 - \frac{\sigma_2}{G} \right)$$

$$W_L \left( 1 - \frac{\sigma_3}{\Delta} \right) = M_L \left( 1 - \frac{\sigma_3}{d_L} \right) + M_P \left( 1 - \frac{\sigma_3}{G} \right)$$

Hence

$$M_L = \left[ W_L \left( 1 - \frac{\sigma_3}{\Delta} \right) - M_P \left( 1 - \frac{\sigma_3}{G} \right) \right] \frac{d_L}{d_L - \sigma_3}$$

And the volume of the pyknometer at  $t_L$  is

$$\begin{aligned} & \frac{M_W}{d_W} \{ 1 + \alpha(t_L - t_W) \} \\ &= \frac{\{ W_W [1 - (\sigma_2/\Delta)] - M_P [1 - (\sigma_2/G)] \} [1 + \alpha(t_L - t_W)]}{d_W - \sigma_2} \end{aligned}$$

Hence

$$\begin{aligned} d_L = & \frac{\{ W_L [1 - (\sigma_3/\Delta)] - M_P [1 - (\sigma_3/G)] \} (d_L / \{ d_L - \sigma_3 \}) (d_W - \sigma_2)}{\{ W_W [1 - (\sigma_2/\Delta)] - M_P [1 - (\sigma_2/G)] \} [1 + \alpha(t_L - t_W)]} \\ & \frac{\{ W_L [1 - (\sigma_3/\Delta)] - W_P \frac{1 - (\sigma_1/\Delta)}{1 - (\sigma_1/G)} [1 - (\sigma_2/G)] \} (d_W - \sigma_2)}{\{ W_W [1 - (\sigma_2/\Delta)] - \frac{1 - (\sigma_1/\Delta)}{W_P [1 - (\sigma_1/G)]} [1 - (\sigma_2/G)] \} [1 + \alpha(t_L - t_W)]} \end{aligned}$$

Making

$$\frac{1 - (\sigma_3/G)}{1 - (\sigma_1/G)} \text{ and } \frac{1 - G}{1 - \sigma_1/G} = 1$$

(by weighing the empty pyknometer immediately before weighing full of water and also before weighing it full of liquid, this equality can be closely achieved experimentally) the last equation becomes

$$d_L = \frac{\{W_L[1 - (\sigma_3/\Delta)] - W_P[1 - (\sigma_1/\Delta)]\}(d_W - \sigma_2)}{\{W_W[1 - (\sigma_2/\Delta)] - W_P[1 - (\sigma_1/\Delta)]\}[1 + \alpha(t_L - t_W)]} + \sigma_3$$

from which

$$d_L = \left[ \frac{W_L - W_P}{W_W - W_P} \right] \left[ \frac{d_W - \sigma_2}{[1 + \alpha(t_L - t_W)]} \right]$$

If the water content and the liquid content are determined at the same temperature,

$$d_L = \frac{W_L - W_P}{W_W - W_P} (d_W - \sigma_2) + \sigma_3$$

If an average value  $\sigma$  is substituted for  $\sigma_2$  and  $\sigma_3$

$$d_L = d_W \left( \frac{W_L - W_P}{W_W - W_P} \right) + \sigma \left( 1 - \frac{W_L - W_P}{W_W - W_P} \right)$$

and if the buoyancy corrections are neglected, the simple approximate relation

$$d_L = d_W \frac{W_L - W_P}{W_W - W_P} \text{ is obtained.}$$

Which of the above equations is used in a particular case is determined by the accuracy of the observations required in the final result; the importance of temperature control in this connexion must not be overlooked.

Similar types of formulae for the density of a solid as determined by the pyknometric method can also be deduced. For very accurate work both with solids and liquids, however, it is advisable to correct to vacuum each of the weighings separately, using the values of the temperature and pressure recorded at the time of weighing, rather than to use one of the above formulae for reducing the final specific gravity to vacuum; this entails more arithmetical labour, but gives more reliable results.

The method of calculation for the density of a liquid is given in the following example; that involved in the determination of the density of a solid by the pyknometric method will at once be obvious from it (cf. Chap. II, S. 5, for a discussion of air corrections in weighing). The same considerations apply to methods depending on the Principle of Archimedes.

*Example :*

Weight of pyknometer	=	31.7426 grams at 16° and 747 mm. pressure
Weight of pyknometer full of water	=	101.6849 grams at 18.5° and 742 mm. pressure
Weight of pyknometer full of liquid under examination	=	157.4127 grams at 19.9° and 739 mm. pressure

These three weights (in grams), corrected for errors in the weights used, become :

31.7492

101.6971

157.4290

The densities of the air at the times of the three weighings are then found by interpolation in the table :

Temp.	Mass of 1 ml. of air at the following pressures in mm.				
	740	750	760	770	780
25°	0.001146	0.001162	0.001177	0.001193	0.001208
20°	0.001168	0.001184	0.001199	0.001215	0.001230
15°	0.001190	0.001206	0.001222	0.001238	0.001254
10°	0.001211	0.001228	0.001244	0.001261	0.001278

The values found are : 0.001197, 0.001178, 0.001166 grams. The weight of the bottle *in vacuo* =  $W_r$ . (The corrected weight of pyknometer =  $W_{a1}$ )

$$\begin{aligned} W_r &= W_{a1}(1 + S.D - S.D') \\ &= 31.7492(1 + 0.001197/2.50 - 0.001197/8.4) \\ &= 31.7599 \end{aligned}$$

Where  $D$  = density of glass, and  $D'$  = density of weights used. The apparent weight of the bottle under the conditions of the other two weighings  $W_{a2}$  and  $W_{a3}$  can now be calculated.

$$\begin{aligned} 31.7599 &= W_{a2}(1 + 0.001178/2.50 - 0.001178/8.4) \\ W_{a2} &= 31.7494 \end{aligned}$$

and 
$$\begin{aligned} 31.7599 &= W_{a3}(1 + 0.001166/2.50 - 0.001166/8.4) \\ W_{a3} &= 31.7495 \end{aligned}$$

The apparent weight of the water can now be obtained :

101.6971 - 31.7494 = 69.9477 ; and that of the liquid  
157.4290 - 31.7495 = 125.6795 ; while the approximate value of the density is  $125.68/69.95 = 1.797$ .

These weights are now corrected to vacuum.

$$W_2 = 69.9477(1 + 0.001178/0.998 - 0.001178/8.4) = 70.0206$$

$$W_3 = 125.6795(1 + 0.001166/1.797 - 0.001166/8.4) = 125.7436$$

and so  $S.G. \frac{20^\circ}{20^\circ} = 1.795809$

and  $D = S.G. \frac{20^\circ}{4^\circ} = 1.795809 \times D_{\text{water}} = 1.795809 \times 0.998230 = 1.792630$

It should be noted that since there are seven significant figures eight figure logs are necessary.

**Disadvantages of the Pyknometer Method.** The three main objections to the pyknometer method, when extreme accuracy is required, are : (a) The difficulty of keeping a large volume of unstirred water at a constant and fixed temperature. (b) The difficulty in removing or correctly allowing for the effects of humidity in weighing the apparatus. (c) The reduction of sensibility of the balance when weighing a relatively heavy load.

The advantages have already been discussed.

**Determination of the Density of a Liquid at its Boiling-point.** Owing to its importance in the study of the influence of chemical structure on physical properties a method of determining the density of a liquid at its boiling-point is here given in detail. The pyknometer used for such determinations consists of a thin glass bulb preferably of Jena glass, capacity 2-3 ml. The bent tube attached is of capillary bore. The tube, after cleaning and weighing, is filled as follows : the bulb is first heated and then

cooled, and immersed in a vessel containing some of the heated liquid of which the specific gravity is required. After a short time the bulb is partly lifted out of the liquid, the open end of the capillary tube being still under the liquid; liquid is thus forced into the bulb as the latter cools. The liquid in the bath is now heated to a higher temperature and the operation of heating and cooling the bulb repeated. This operation is carried out several times with the bath at a higher temperature each time. The bulb is finally obtained full except for a minute air-bubble. Sometimes filling is done by placing the apparatus in a small vessel which can be partially exhausted, and by dipping the open end of the capillary under the liquid contained in the vessel. On allowing air to enter the latter, some liquid will have entered the pyknometer. This operation is repeated several times until the bulb is practically full.

The pyknometer is suspended by a platinum wire in a wide-mouthed boiling flask so that it is just above the surface of the liquid (this liquid being the same as that in the pyknometer). The flask is next heated until the liquid it contains is raised to its boiling-point. With the increase in temperature, the liquid in the pyknometer expands, and all the small air-bubbles are expelled; the boiling is stopped when the pyknometer and its contents have reached a constant temperature; the apparatus is then quickly cooled and the pyknometer dried and weighed. To make allowance for the changes with temperatures in the volume of the apparatus, it is necessary to know the weight of the pyknometer empty and also its weight full of water at two temperatures.

If the pyknometer contains  $v$  ml. water ( $wt$ ,  $w$  grams) at temp.  $t$ , and  $v^1$  ml. water ( $wt$ ,  $w^1$  grams) at temp.  $t^1$ , and  $v_\theta$  ml. of liquid ( $wt$ ,  $w_\theta$ ) of which the density (i.e.  $\Delta_\theta$ ) is required at temp.  $\theta$  (boiling-point of this liquid), then if  $\alpha$  = linear coefficient of expansion of glass,

$$\begin{aligned} v^1 - v &= 3\alpha v(t^1 - t) \\ v_\theta - v &= 3\alpha v(\theta - t) \\ v_\theta - v &= (v^1 - v) \frac{(\theta - t)}{(t^1 - t)} \\ &= k(\theta - t) \text{ where } k = \frac{(v^1 - v)}{(t^1 - t)} \\ \Delta_\theta &= \frac{w_\theta}{v_\theta} = \frac{w_\theta}{v + k(\theta - t)} \end{aligned}$$

For accurate work buoyancy corrections for weights will have to be introduced. This involves a knowledge of the density of any vapour in which the pyknometer is suspended. Such accuracy, however, is seldom required in work of this kind.

**Displacement Methods.** All these methods are based on the Principle (Archimedes) that a solid when immersed in a liquid displaces its own volume of that liquid. For the most part the manipulation and calculations involved are not dissimilar to those which have been described in connexion with the application of this principle to the determination of the density of a solid body.

**Use of a Hydrometer.** For rapid and fairly accurate determinations

the ordinary hydrometer is most convenient and is most frequently used in industry. It consists (Fig. 20 (XII)) of a glass bulb weighted with a little mercury and fitted with a graduated stem. If immersed in a liquid at a standard temperature the depth to which it floats gives at once the required density to about the third decimal place. For laboratory work a range of hydrometers, each covering about 2 units in the first decimal place and graduated to the third decimal place, is convenient. Fig. 21 (XII) shows a Sikes hydrometer suitable for density determination over various ranges.<sup>1</sup>

Nicholson's hydrometer can also be employed to determine the density of a liquid; the weights with which the upper pan must be loaded to sink it to the fixed mark in a liquid of known density and in the liquid under observation are determined.

**Recording Hydrometers.** For industrial use hydrometers are readily made self-recording by providing a drum driven by clockwork on which is marked the level of a fixed point on a hydrometer floating in a liquid of varying density but with its surface level fixed.

**Direct Weighing Methods.** If a sinker of glass or other suitable substance be weighed in air, in pure water at a fixed temperature and in the liquid under observation, the density of the latter can at once be calculated (Fig. 22 (XII)).

This static method was employed by Osborne, McKelvey and Bearce<sup>2</sup> with results in very good agreement with pycnometer determinations. The

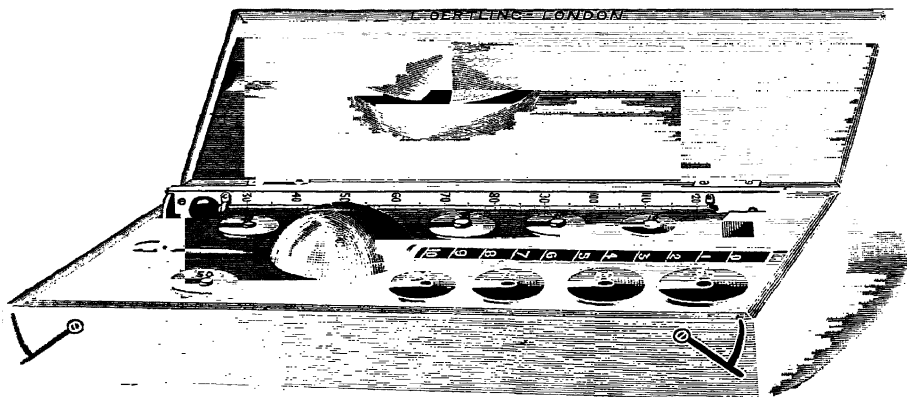


FIG. 21 (XII)

sinker used was of Jena glass and was 33 cm. long and 1.3 cm. external diameter; it was ballasted with mercury, and before sealing was well

<sup>1</sup> Electros for Figs. 20 (XII) to 22 (XII) kindly supplied by Messrs. L. Oertling, Ltd., London.

<sup>2</sup> *Bulletin Bureau of Standards (U.S.A.) Reprint, 197.*

annealed at  $450^{\circ}$ . The sinker was suspended, by means of a platinum wire, 0.3 mm. in diameter, in the very slightly larger densimeter tube, and was attached to the bottom of one pan of a good balance standing on a shelf above the thermostat. The wire was covered, by electro-deposition, with a layer of dull gold at the point where it entered the liquid. This device was found to ensure the wetting of the suspension and the prevention of slight sticking, which otherwise (due to surface tension) would occur. Platinum black on the fine platinum suspension wire has also been used. These devices reduce surface-tension effects, but do not completely eliminate them. To the wire was attached a plug which fitted into a hole in the top of the densimeter cover, and the proportions were so arranged that when the balance was arrested the plug filled the hole, while the sinker just rested on

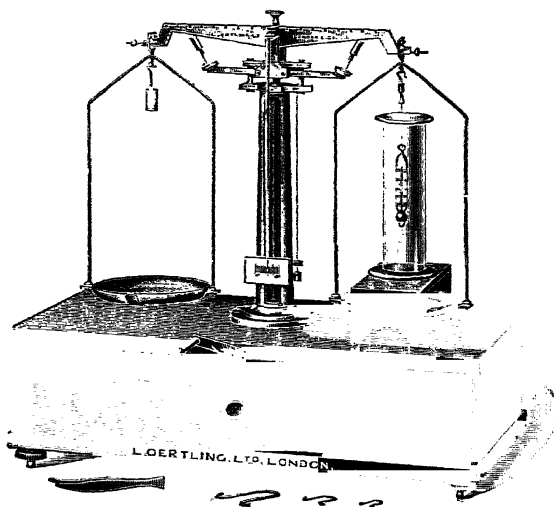


FIG. 22 (XII)

the bottom of the densimeter. When the beam was released the sinker was raised off the bottom, and, the plug being removed from the hole, left the sinker freely swinging. By this means the liquid was only exposed to the air during the actual weighing. The chief difficulties were due to alteration of the concentration of the solution by evaporation and by absorption of water from the air. Also, unless the liquid was first carefully freed from dissolved air, small bubbles formed on the sinker which could not easily be removed. These writers state that the density of alcohol is altered by eight in the fifth place by saturation with air at  $25^{\circ}$ . The volume of the sinker was first determined by weighing it in air and then in air-free distilled water; then by making use of the known densities of the air and of the water, its volume was obtained. Next, the sinker was weighed in the liquid, and, having been removed, the suspension was weighed and the sinker was replaced and again weighed: the mean value of the difference gave the



apparent weight of the sinker in the liquid. The density was calculated from the expression

$$D'_1 = \frac{S - W_1 - w + W_2 - W}{2 V_t} \left( 1 - \frac{d}{8.4} \right)$$

where  $S$  = the mass of the sinker  
 $V_t$  = the volume of the sinker at  $t^\circ$  (the temperature of the thermostat)  
 $W$  = weight of suspension  
 $W_1$  and  $W_2$  = balance readings with the sinker on  
 $w$  = balance reading with the sinker off  
 $d$  = the density of the air

This method is particularly useful for following the variations of the density of a liquid with temperature : the liquid under observation is placed

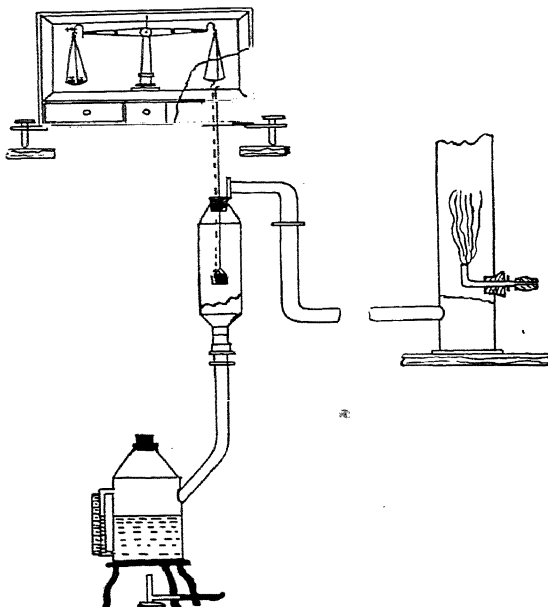


FIG. 23 (XII)

in a vessel surrounded by a thermostat, and the balance is mounted above this. Fig. 23 (XII) shows such an apparatus. The draught caused by a flame draws vapour around the vessel containing the liquid.

**Mohr-Westphal Balance.** This is a well-known apparatus, easy to manipulate and giving results accurate to the fourth decimal place. It is of use both in the laboratory and industrially. It depends on the variation in weight of a sinker when immersed in liquids of different densities and

consists (Fig. 24 (XII) ) of a balanced arm on an adjustable stand to which the sinker is attached by means of a fine wire, preferably of platinum.

This sinker is suspended in pure water and a horse-shoe weight is attached to the sinker hook. A slight adjustment of the counterpoise produces equilibrium. Weights 0.1, 0.01, 0.001 of the larger weight are also provided, and the arm from which the sinker hangs is divided into ten equal parts. So when the sinker is suspended in the liquid under test, assumed less dense than water, its density compared with water at the same temperature for which the instrument has first been adjusted is obtained by determining the position of the arm from which the given weights must be hung to produce equilibrium. Thus, if the first weight was 0.8 of the total length of the arm from the fulcrum, the next 0.6, the third 0.7, and the fourth 0.3, the density of the liquid compared with water at the same temperature would be 0.8673; its density compared with water at any other temperature can at once be calculated.

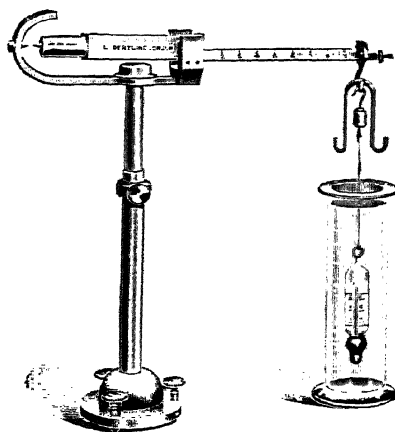


FIG. 24 (XII)

The balance must be adjusted for water at the temperature at which the liquid is to be examined to eliminate errors due to the change in size of the sinker. A special glass container, with a mark to which the liquid is to be filled (to ensure the same length of wire is always immersed in it), is provided together with a thermometer which is sometimes incorporated with the sinker. The whole apparatus is constructed so that it can readily be dismantled and packed securely in a portable box.

For liquids heavier than water, weights multiples of the standard weight are employed. No correction is needed for the surface tension effect of the platinum wire, as this quantity is smaller than the experimental error.

**Totally Immersed Floats.** The displacement or hydrostatic method has not the three drawbacks which the pyknometer method already mentioned possesses. The liquid can be kept at a constant temperature, as it is possible for it to be stirred. The humidity effects do not interfere, as the float is surrounded by the liquid at constant temperature and so a definite surface condition will result. Thirdly, the load on the balance is small, since the weight of the float is neutralized by the buoyant effect of the liquid. To overcome the surface-tension effects caused by the wire in the suspension method, a submerged sinker of known specific gravity can be employed and distilled water added until the sinker hovers in the liquid, or small platinum weights are attached to the sinker until the same state is obtained. Alternatively, temperature can be made the variable factor and results obtained correct within 1 in 5,000,000. It is difficult, however, to vary the buoyancy of the sinker by very small amounts (variations as small as 0.01 milligram

being necessary), while slight temperature alterations are also difficult to accomplish. Lamb and Lee have devised an extremely accurate apparatus in which they have avoided these difficulties. They place a piece of soft iron in the bulb of the sinker and by means of an electric current sent through a properly-placed external circuit exert a known electro-magnetic attraction in a vertical direction upon the bulb, and thus produce displacement of the sinker in a vertical direction. This attraction produces the effect of added weights. The error of the method, it is claimed, is less than one unit in the seventh decimal place.

An application of this method by which densities can readily be obtained with fair accuracy is to add to a liquid a number of glass beads of known densities and to observe which float and which sink. This method is similar in principle to Retgers', referred to elsewhere.

The same principle has been used by Bishop<sup>1</sup> to check or replace the specific gravity method. The liquid is contained in one of a pair of double-walled vertical tubes, used alternately, and filled and emptied at the bottom by means of a suction pump. The tubes which contain thermometers are in the form of an inverted cone at the bottom, a solenoid being wound on this portion, so that a current flowing through the wire exerts an electro-magnetic attraction on a hollow soft-iron float in the liquid and causes it to sink. If the current is then gradually reduced until the float just begins to rise again its strength at this point is a measure of the specific gravity of the liquid.

**Hare's Method.** In this method two liquids are caused to rise in the limbs of a U-tube by reducing the pressure in the upper portion of the tube. A stopcock is then closed, when the lengths of the columns of liquid in the two tubes will be inversely proportional to the densities of the liquids, so that if the density of one be known that of the other follows.

A very sensitive application of the above principle has been developed by Frivold.<sup>2</sup>

Briscoe and his co-workers<sup>3</sup> claim that the flotation method of density determination is more precise than the pycnometric method for comparisons of densities of heavy water.

<sup>1</sup> *J. Inst. Brew.*, 1934, 40, 92.

<sup>2</sup> *Phys. Zeit.*, 1920, 39, 529.

<sup>3</sup> *J. Chem. Soc.*, 1934, 145, 1207.

## SECTION 4: COEFFICIENT OF THERMAL EXPANSION

**Solids, Linear Expansion.** If the distance between points in a solid body at  $0^\circ$  is  $l_0$  and at  $t^\circ$  is  $l_t$ , and if  $l_t = l_0 (1 + \alpha t)$ ,  $\alpha$  is usually positive and is called the coefficient of linear expansion between  $0^\circ$  and  $t^\circ$ . It is not a constant but varies somewhat with temperature. It is a very small quantity, being of the order  $10^{-5}$ .

To determine such a small quantity, two methods are in use. In one a comparator is employed—the distance between two fixed marks on a bar heated to different temperatures, e.g. by suitable vapour baths, is determined as described in Chapter II, § 1. In the other method, due to Fizeau, interference fringes are used to provide a scale. The latter method can be used with small quantities of material. For the determination of the coefficient of linear expansion (i) the method of the optical lever, or (ii) a single travelling microscope can be used.

**Area and Volume Expansion.** If a square length of side  $l_0$  be marked out on a body at  $0^\circ$  then if  $\beta$  be the coefficient of expansion of area as above

$$\begin{aligned} l_t^2 &= l_0^2(1 + \beta t) \\ &= l_0^2(1 + \alpha t)^2 \end{aligned}$$

and since  $\alpha$  is small

$$= l_0^2(1 + 2\alpha t)$$

Hence  $\beta = 2\alpha$  and if  $\gamma$  is the coefficient of cubical expansion defined on similar lines

$$\gamma = 3\alpha$$

It is assumed that the body under investigation is uniform in all directions.

Hence, with such a body it is possible to determine  $\alpha$  and  $\beta$  if  $\gamma$  is known. And since this quantity is most readily determined, it is used to establish the other two except in very accurate work.

Crystals, however, which do not belong to the regular system have slightly different coefficients of linear expansion in different directions, and direct measurements of  $\alpha$  are then necessary.

**Measurement of Volume Coefficient.** The volume coefficient is the most important of the three coefficients. It can be obtained by any of the methods described for density determinations, since a knowledge of how the density of a body varies with temperature at once gives the variation in volume of a given mass. The dilatometer method and methods involving the Principle of Archimedes are of particular value in this connexion.

**Liquids.** With liquids the volume coefficient is the only one to be considered, and as with solids, the methods used for density determinations are here applied. There is one other related method, the weight-thermometer method, which, although it can be employed to determine the change

in density of a liquid, is more usually applied to measure accurately its volume coefficient as such; it is, so to speak, a weight dilatometer, and is more accurate than a volume dilatometer, which is however often employed.

**The Weight-thermometer.** This consists of a vessel of the shape shown in the figure (Fig. 25 (XII)) constructed of glass or preferably amorphous silica. It is completely filled with the liquid under examination by alternate heating and cooling, while the open end is immersed in the liquid in a porcelain crucible; it is of advantage to boil the liquid in the vessel when the filling is nearly complete. The thermometer is then heated to various temperatures with the open end dipping under liquid in the

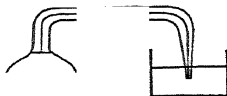


FIG. 25 (XII)

crucible, and after equilibrium has been attained it is cooled and weighed. The vessel is also weighed empty. The method of calculation of the coefficient of volume expansion of a liquid or of the density at various temperatures will be obvious. It is necessary to know the coefficient of cubical expansion of the material of the vessel: if silica, for which  $\gamma$  is very small, is employed, the errors due to the difficulty of measuring this quantity accurately are much reduced, e.g. for silica  $\gamma$  equals  $15 \times 10^{-7}$ ; while for glass it is  $27 \times 10^{-6}$ ; for mercury it is  $18.2 \times 10^{-5}$ . Further, silica is much easier to manipulate, since there is no danger of its cracking owing to sudden changes in temperature.

This method is of course closely related to the pycnometer method for density determination. Its name is derived from the fact that with a liquid for which  $\gamma$  is accurately known, temperatures can be determined by its use.

**True and Apparent Coefficient of Expansion of Liquids.** If the coefficient of expansion of a vessel is appreciable, that of the liquid contained in it is not accurately observed owing to the expansion of the vessel on heating. The observed coefficient of expansion of the liquid is less than the true coefficient by an amount equal to the coefficient of expansion of the glass, as will be seen from the following considerations:

Let  $V$  ml. be the volume of the liquid filling the vessel before heating,  $v$  ml. the volume of liquid overflowing when the vessel is heated through a known range of temperature, and

$x$  = true coefficient of expansion of the liquid  
 $a$  = apparent        "        "        "  
 $g$  = coefficient        "        "        glass

Then volume of liquid remaining in containing vessel after heating =  $V(1 + g)$ . The apparent coefficient of expansion of the liquid is therefore

$$a = \frac{V(1 + g) + v}{V} - 1 = \frac{v}{V} + g$$

But the true increase of volume of the liquid is

$$V(1 + g) + v = V(1 + g) + Va(1 + g) = V(1 + x)$$

where  $x$  is the true coefficient of expansion of the liquid. So that

$$V(1 + g)(1 + a) = V(1 + x)$$

$$\text{whence } x = a + g + ag$$

The product  $ag$  is too small to be taken into account, and

$$x = a + g$$

**Dulong and Petit's Method.** This method has been used in certain investigations, since it is the only method for liquids which does not involve the coefficient of expansion of the containing vessel. It is related to Hare's method, there being employed two tubes of liquid (Fig. 26 (XII)), each of which is maintained at a different temperature, and the heights of the columns compared. The experimental difficulties are however great and the method is employed only in fundamental physical work. Fig. 26 (XII) is simply a diagrammatic representation of this method. For improved apparatus, see later.

Callendar and Moss improve the accuracy of this method by using 6 pairs of hot and cold columns each 2 metres long and connected in series. For comparison of various experimental methods applied to mercury, see *Phil. Mag.*, 1929, 1, 674.

**Hydrostatic Balance Method.** Such a balance may be employed for the total expansion of a solid. An ordinary balance may also be employed. Over one pan is placed a bridge on which a jacketed heater containing liquid is placed. The solid of which the coefficient of expansion is known, is weighed in air and then in the liquid (i) at laboratory temperature, and (ii) at a higher temperature. If the weight in air is  $A$  and the apparent weights  $A_1$  and  $A_2$  at the two temperatures  $t_1$  (lab.) and  $t_2$  (higher temp.), then  $A - A_1 =$  weight of a quantity of the liquid which has the same volume as the solid at temp.  $t_1^\circ$  and  $A - A_2 =$  the weight of a quantity of liquid which has the same volume as the solid at  $t_2^\circ$ . These weights correspond to the weights of the liquid which at  $t_1^\circ$  and  $t_2^\circ$  respectively would fill a weight thermometer made of the material of the solid. The total expansion can be found in the same way as from the weight thermometer experiment.

**Coefficient of Expansion of Water.** With most liquids  $\gamma$  is positive and greater than  $\gamma$  for solids. Between  $0^\circ$  and  $4^\circ$ , however,  $\gamma$  for water is, as is well known, negative. No satisfactory explanation for this has as yet been put forward.

**Effect of Pressure.** The effect of pressure on the density and coefficient of expansion of solids and liquids can be demonstrated but since for ordinary pressures it is very small it has not been necessary to discuss it.

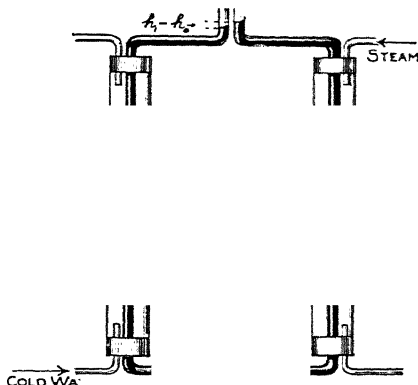


FIG. 26 (XII)

## SECTION 5: SURFACE TENSION <sup>1</sup>

**Mechanism of Surface Tension.** On the molecular theory of matter each molecule within a liquid attracts and is attracted by surrounding molecules. The attracting force may be assumed to be negligible when the distance between the molecules exceeds a certain small value. Each molecule may thus be pictured as surrounded by a sphere of attraction. Forces then exist between each molecule and other molecules within its sphere of attraction. In the body of a liquid the resultant of these forces is zero, since each molecule is completely surrounded by similar molecules; in the surface layer this does not hold, as the molecules in the upper half of the sphere of attraction are comparatively few. Consequently the free surface of a liquid behaves as if it were in a state of stress. Forces act across the surface which are the direct result of molecular attraction and consequently their measurement is of importance. If a straight line 1 cm. in length be drawn in the surface of the liquid in contact only with its own vapour, then the force across this line at right angles is defined as the *surface tension* of the liquid. Surface tension is thus a force per unit length.

For the moment to avoid confusion with the Time unit, let this force per unit length be denoted by  $x$ ; then if the line of unit length be moved unit distance at right angles to itself in the surface, the work done will be  $x$ , so that it may be measured also as energy per unit area.

**Surface Tension Equation.** Surface Tension, molecular volume and temperature are related according to the formula first discovered by Eötvös

$$TV^{\frac{2}{3}} = a(\theta_{\kappa} - \theta)$$

where  $T$  = surface tension in dynes per centimetre or ergs per square metre

$V$  = the molecular volume

$\theta_{\kappa}$  = the critical temperature on the absolute scale

$\theta$  = the absolute temperature at which  $T$  and  $V$  were measured

$a$  = a constant

The Ramsay and Shields correction changes the formula as follows:

$$TV^{\frac{2}{3}} = a(\theta_{\kappa} - \theta - \delta)$$

the value of  $\delta$  is approximately 6 and the constant  $a$  for a number of liquids examined was 2.12. It is now known, however (see Chap III), that Ramsey and Shields underestimated the capillary rise, so that the last term ( $\delta = 6$ ) is not justified.

M. Katayama <sup>2</sup> employs the difference of the densities of liquid and

<sup>1</sup> See page 109.

<sup>2</sup> Masao Katayama, *Sci. Report*, Tohoku Univ., 1916, IV, 5.

vapour in the equation of Eötvös instead of liquid density and obtains :

$$D_p \frac{M}{D_g} = a(\theta_\kappa - \theta)$$

$$a = 2.04$$

$M$  = the common molecular weight

$D_p$  = liquid density

$D_g$  = vapour density

This formula, it is claimed, agrees better with experimental results than that of Ramsay and Shields.

**Interfacial Tension.** Where the free surface of the liquid is not in contact with its own vapour alone, the force measured is really the *interfacial tension* of the liquid with the surrounding matter. Thus the interfacial tension varies as the surface is in contact with a gaseous, liquid, or solid medium. Where the liquid surface is in contact with its own vapour mixed with air the interfacial tension does not differ from the surface tension by more than 0.5 per cent. This is the tension usually measured, the conditions for the measurement of the true surface tension being very difficult to attain. The latter constant is thus seen to be a particular case of the general interfacial phenomena.

**The Parachor.**<sup>1</sup> Many attempts have been made to find an accurate relation between the molecular surface energy  $\gamma(Mv)^{\frac{1}{3}}$ , where  $\gamma$  is the surface tension,  $M$  the molecular weight, and  $v$  the specific volume, and temperature (Eötvös, Ramsay and Shields, &c.). Two formulae which, for non-associated liquids, give results in good agreement with experiment are

$$\text{Ferguson's} \quad \gamma = \gamma_0(1 - T_r)^{1.2}$$

where  $T_r$  is the reduced temperature and

$$\text{Macleod's} \quad \gamma = K(D - d)^4$$

where  $K$  is a constant,  $D$  is the density of the liquid, and  $d$  that of the gas at the temperature of the experiment.

Sugden tested these two equations and for the second one obtained the following results :

$\gamma^{\frac{1}{4}}(D - d)$ = $K^{\frac{1}{4}}$			$\gamma^{\frac{1}{4}}(D - d)$ = $K^{\frac{1}{4}}$		
$C_6H_6$	20	2.637	$C_6H_5Cl$	12	2.166
	120	2.643		150	2.174
	240	2.657		300	2.169
$CCl_4$	20	1.429			
	180	1.429			

i.e. the values of  $K^{\frac{1}{4}}$  show great constancy.<sup>2</sup>

<sup>1</sup> From Rae and Reilly, *Physico-Chemical Practical Exercises* (Methuen), London, 1934.

<sup>2</sup> See, however, page 110.



Sugden defined a term, the parachor  $P$ , by the equation

$$P = M \cdot K^{\frac{1}{4}} = \gamma^{\frac{1}{4}} \times M / (D - d)$$

$M$  being the molecular weight; at low temperature  $d$  is negligible and  $M / (D - d)$  is equal to the molecular volume ( $M \cdot v$ ). Hence for two liquids

$$\frac{P}{P_1} = \frac{\gamma^{\frac{1}{4}} \cdot M \cdot v}{\gamma_1^{\frac{1}{4}} \cdot M_1 v_1}$$

and if the liquids are compared at temperatures where their surface tensions are equal, the parachors are proportional to the molecular volumes at these temperatures.

The parachors of the elements are additive quantities and can be calculated in a similar way to that used in the case of molecular volumes, so that the effect due to each element and of constitution can be found. For example :

n. hexane $C_6H_{14}$	$P = 270.1$	
n. heptane $C_7H_{16}$	$P = 309.3$	
difference for $CH_2$	$= 39.2$	(mean value = 39.0)
propane $C_3H_8$	$P = 150.8$	
$3 \times CH_2 = C_3H_6$	$= 117.0$	
difference for $2H$	$= 33.8$	
and for $H$	$= 16.9$	(mean value = 17.1)
$CH_2$	$P = 39.0$	
$2H$	$= 34.2$	
therefore $C$	$= 4.8$	

Some of the results obtained are

$C = 4.8$	triple bond	$= 46.6$
$H = 17.1$	non-polar double bond	$= 23.2$
$O = 20.0$	semi-polar double bond	$= - 1.6$
ester $O = 60.0$	singlet	$= - 11.6$
$N = 12.5$	semi-polar single bond	$= - 12.4$
$Cl = 54.3$	{ 5 membered ring	$= 8.5$
	{ 6 membered ring	$= 6.1$

The effect of constitution is therefore seen to be very marked, e.g. with benzene,

$$\begin{aligned}
 6 \times C &= 28.8 \\
 6 \times H &= 102.6 \\
 3 \text{ double bonds} &= 69.6 \\
 6 \text{ membered ring} &= 6.1 \\
 \text{therefore } P &= 207.1
 \end{aligned}$$

Experiment gives at  $17.5^\circ$

$$\begin{aligned}
 \gamma &= 29.2 \\
 \gamma^{\frac{1}{4}} &= 2.324 \\
 D &= 0.8815
 \end{aligned}$$

$$\text{therefore } P = \frac{2.324 \times 78}{0.8815} = 205.6$$

**Reliability of Measurements.** The measurement of interfacial tensions has been accomplished by a great variety of methods. Grave doubt is entertained of the results achieved by some of these. Ferguson<sup>1</sup> gives a critical survey of the reliability of the existing methods. In these papers doubt is cast on some of the better-known methods, such as the capillary-rise method, Wilhelmy's method, and the drop-weight method, owing to their dependence on the angle of contact and the corresponding assumption that for liquids which wet glass this angle is zero. The later work of Richards and Carver vindicates this assumption, as these workers have shown that most of the common liquids which wet glass have zero angle of contact if the glass is perfectly clean and the liquids are pure. Under these conditions the methods enumerated may be considered reliable.

Lecomte du Noüy has worked out a reliable method for the measurement of the surface tension of very small quantities of liquids by the ring method. The procedure adopted has been extensively applied in investigations on the surface equilibria of colloid solutions. Tests have been carried out on serum solutions, on colloidal solutions of metals and on the size of various molecules, e.g. egg albumin and sodium oleate. The results are in agreement with other physical measurements.

**General Precautions.** In carrying out measurements of this nature it is essential to work with thoroughly clean apparatus or very serious errors may occur. Glass or liquid surfaces should not be left exposed to the air for any time; in making a series of measurements the working surfaces should, if possible, be cleaned between each measurement; the usual cleaning sequence, chromic acid, water, alcohol and ether may be used.

**Methods.** Of the many methods which have been devised for the measurement of surface tension, two only have been used to any extent in physico-chemical work. This is largely due to the fact that most methods which are otherwise satisfactory do not lend themselves to accurate temperature control (e.g. the method of the wave-length of ripples), and since the temperature effect is appreciable, accurate temperature control is necessary. The two which have been most largely used are the capillary-rise method and the falling-drop method. The former depends upon the fact that when a capillary tube is dipped into a liquid, the liquid rises to a height ( $h$ ) in the tube given by the relation

$$2T \cos \omega = rg(\rho - \sigma)(h + x)$$

where  $T$  is the surface tension in dynes per centimetre

$\omega$  is the angle of contact of the liquid with the walls of the tube

$r$  is the radius of the capillary tube in centimetres

$g$  is the acceleration due to gravity in centimetres per second per second.

$\rho$  is the density of the liquid, and  $\sigma$  that of the vapour or gas with which it is in contact

$x$  is a correction factor for the liquid above the level of the bottom of the meniscus of the liquid in the tube

<sup>1</sup> *Science Progress*, 1914, 428; and 1921, 365. Cf. also Rae and Reilly, *Science Progress*, 1920, 58, 223-233.

The data given in Landolt-Börnstein's tables show that the values obtained by different experimenters for the surface tension of water at 20° by the capillary-rise method vary between 70.6 and 72.7, while the values by all methods vary between 70.6 and 78. Thus, although a single experimenter gets values which agree very well among themselves, they may differ by 3 per cent from those of other workers. It is also noteworthy that the capillary rise results are generally lower than those obtained by other methods.

**Errors in Measurement.** Before describing the method of measurement it will be well to consider the causes of the discrepancies pointed out above. Willard Gibbs has shown that, in order to keep the potential energy of the system at a minimum, a solute which diminishes the surface tension will be concentrated in the surface layer, while a solute which raises the surface tension will have a lower concentration in the surface layer than in the main bulk of the liquid. Now the surface layer in a capillary tube has very small dimensions, and thus a very minute trace of impurity, which lowers the surface tension, is capable of giving a high concentration in this very small surface, and in consequence may produce a lowering of the surface tension altogether out of proportion to its mass.

The height  $h$  given in the formula represents the distance of the meniscus in the tube above the flat surface in the outer vessel. It is probable that one of the chief reasons for the variations between the results of different observers lies in the fact that they have assumed the surface in the outer tube to be flat, which is not the case. The question has been considered by Richards and Coombs; they showed that in a tube 2 cm. in diameter with a thin rod in the centre, water rose 0.31 mm. higher than in tubes on either side without the central rod; they found experimentally that a tube 3.8 cm. in diameter gave a flat surface at its centre, all the capillary rise taking place at the edges. Lord Rayleigh calculated that the minimum diameter for a flat surface would be 4.7 cm. It should be noticed that these values refer to tubes without a capillary tube in the centre, such as there is in the ordinary arrangement of, say, Ramsay and Shields' apparatus; with this arrangement a still wider tube would be required.

In calculating the height to which the liquid is raised a correction has to be employed for the liquid contained in the meniscus above the lowest point (where the measurement is made). In very narrow tubes the surface of the liquid is practically hemispherical, and the volume of the liquid is then the difference between the volume of a cylinder of height  $r$  and that of a hemisphere of radius  $r$  (i.e.  $\pi r^3 - \frac{2}{3}\pi r^3 = \frac{1}{3}\pi r^3$ ), so that the correction is made by adding one-third of the radius of the tube to the observed height  $h$ . A more exact relation has been worked out by Poisson for tubes of small radius, who found

$$2T/g\rho r = h + r/3 - 0.1288r^2/h$$

This result has been confirmed and extended by Lord Rayleigh, who gives

$$2T/g\rho r = h + r/3 - 0.1288r^2/h + 0.1312r^3/h^2$$

where  $\rho$  = the density of the fluid.

Richards and Coombs measure the height  $h_m$  of the capillary meniscus and use the expression  $h = h_0 + n \cdot h_m$ , where  $h$  = the true corrected height

and  $h_0$  the observed height and where  $n$  varies from 0.3 for tubes 2 mm. in diameter to 0.25 for tubes 30 mm. across.

**Capillary-rise Method.** The first step in setting up an apparatus for the measurement of surface tension by the capillary-rise method consists in the preparation of a capillary tube of uniform bore. A piece of glass tubing about 1 cm. in diameter and fairly thick-walled is chosen; this is heated to redness at the centre until it softens. An assistant holding one end then walks rapidly away until the tube is pulled out to a length of 10 or 12 feet. The central part of the capillary is cut into lengths of about 10 cm., and these are examined for uniformity. The capillary tubes can be cleaned by making a pin-hole in a piece of rubber tubing, one end of which is closed by a piece of glass rod and the other is attached to the water pump; one end of the capillary is pushed into the pin-hole, and the other is placed in a beaker containing the cleaning liquid, which is thus sucked through the tube, the usual liquids—chromic acid, distilled water, alcohol and ether—being used. A thread of clean mercury is then drawn into the tube, and its length is measured at various points in the tube by laying it alongside a standard scale on a microscope giving good magnification. A tube should be rejected which shows a variation in the length of the thread of more than 1 in 1,000. When a satisfactory tube has been found, the length of the thread is recorded for the position nearest to which the meniscus will be formed, and the mercury is run out and weighed. The radius of the tube can then be calculated from the equation  $r = \sqrt{m/\pi \rho l}$ , where  $m$  is the mass of the mercury,  $\rho$  its density at the room temperature, and  $l$  the length of the thread corrected for the meniscus at each end by a quantity which can be calculated. By means of a very fine sharp file, a small ring is then cut off the end of the capillary and is placed on the stage of a microscope with a micrometer eyepiece, and the diameter is measured in four directions at  $45^\circ$  to find if it is truly circular, the same standard as before being required. If the cross-section is found to be satisfactory, a divided millimetre is placed on the stage, and the micrometer readings are reduced to millimetres. The diameter thus found can be compared with that found by weighing the mercury, the preference being given to the direct measurement in case there is any slight difference. Ramsay and Shields then proceeded as follows: A short tube of thin-walled glass, containing a spiral of iron wire, was sealed on to a short piece of glass rod 1 mm. in diameter. The capillary was dipped in ether, inclined so as to fill it with the liquid, and one end was sealed; the open end was then held so as to touch the glass rod, and a very small pointed flame was directed on to the junction; the glass was then sealed on, and the vapour pressure of the ether blew a small bulb at the bottom of the capillary and a minute hole in the side of the bulb. The sealed end was cut off for the determination of the radius. The capillary was placed in the wider tube and the liquid was added. The wider tube was constricted at the top and attached to the pump in order to boil out all the air; it was then sealed off at the narrow portion. Thus Ramsay and Shields' determinations were all made with the liquid in contact with its own vapour (Fig. 27 (XII)). Renault and Guye used the same method, but carried out their determinations in the presence of air as being much simpler—the difference in the values obtained was about 0.5 per cent. In carrying out a determina-

tion, a scale was attached to the front of the wider tube and this was placed in a vapour-bath. The capillary could now be lowered by means of the attraction of the electro-magnet on the iron wire spiral attached to its lower end. It was lowered so as to allow the liquid to flow over the top, thus renewing the surface before each reading and ensuring the wetting of the glass above; the meniscus was then raised until the latter came to a point 2 mm. below the end of the tube, and the height was read by means of a cathetometer and the scale in front of the glass. As an example of Ramsay and Shields' results, with carbon disulphide as the liquid and  $r = 0.0129$  cm., they obtained:

At $t = 19.4^\circ$	At $t = 46.1^\circ$
$h = 4.21$ cm.	$h = 3.80$ cm.
$h = 4.20$ cm.	$h = 3.795$ cm.
$h = 4.20$ cm.	$h = 3.80$ cm.
Mean $h = 4.203$ cm.	Mean $h = 3.798$ cm.
Density ( $d_1$ ) = 1.264 (grams per ml.)	Density ( $d_2$ ) = 1.223 cm. (grams per ml.)

$$\text{Surface Tension (T)} = \frac{1}{2}grdh$$

$$T_1 = 33.6 \text{ dynes per sq. cm.} \quad T_2 = 29.4 \text{ dynes per sq. cm.}$$

They then used these values to calculate  $\frac{dT(Mv)^{\frac{2}{3}}}{dt}$

which is the molecular surface energy (where  $v$  is 22.32 litres for a normal gas and  $M$  is the gram molecular weight).

$$T_1(M/d_1)^{\frac{2}{3}} = 33.6(76/1.264)^{\frac{2}{3}} = 515 \text{ ergs}$$

$$T_2(M/d_2)^{\frac{2}{3}} = 29.4(76/1.223)^{\frac{2}{3}} = 461 \text{ ergs}$$

Then

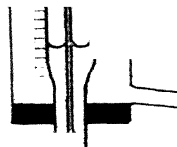
$$\frac{dT(Mv)^{\frac{2}{3}}}{dt} = \frac{515 - 461}{46.1 - 19.4} = \frac{54}{26.7} = 2.02$$

The defect of the apparatus consists in the fact that the outer tube is not sufficiently wide to ensure that there is no capillary rise there, thus making the result too low. The apparatus used by Richards and Coombs is more accurate (Fig. 28 (XII)). The capillaries were carefully selected according to the method already described. In one form the diameters of the narrow and wide tubes were 0.20198 and 3.8 cm. respectively, and in the second 0.01936 and 3.8 cm.; the volume of the liquid required for the first tube was 36 ml., but this was reduced to 12 ml. in another form by means of the sinker. A reference mark was etched near the centre of the capillary. Particular care should be taken, when

using apparatus containing stopcocks, to make certain that these are thoroughly clean; they can only be lubricated with the liquid in the tube, and, so as to prevent the entrance of the water, the outside of the tap is



D



G

FIG. 27 (XII)

covered with a film of paraffin before the apparatus is placed in the bath. The method used to observe the position of the meniscus with accuracy was to set the apparatus vertically with a plumb-line in the thermostat (which had parallel plate-glass sides). A black metal screen having a rectangular hole in it, with the horizontal edge quite straight, was lowered into the thermostat so as to lie just behind the apparatus, and was then adjusted so that the straight edge was just horizontal, and when viewed through the cathetometer, appeared to make a tangent with the lowest point of the meniscus. The upper edge of the meniscus could also be determined when desired by gradually raising the plate, whereby the line of the straight edge at first appears broken, but when it reaches the top of the meniscus again appears to be straight. Before using the apparatus it was carefully calibrated with water in the following way: The apparatus was first thoroughly cleaned, and was then filled with water so that it reached a position below the reference mark. The water was then run up and down the capillary several times, and the apparatus was set vertically with the plumb-line and the height read; the tube was again wetted, turned through  $180^\circ$ , and the height again read (always allowing for the liquid to drain and reading with a falling thread); next the tube was inverted, and the two readings were repeated. More water was added and new readings were taken, and so on. To show the kind of values obtained, the following figures represent the mean of five readings in each position: 1.4378, 1.4422, 1.4384, 1.4391 cm. The mean of these is 1.4394, with a probable error of 0.03 per cent. By proceeding in this way it was found, for example, with one tube, that the most constant results were obtained within the region 0.4 to 1.3 mm. of the reference mark, and this part of the capillary was therefore used in the actual determinations. The surface tension of benzene was obtained at  $20^\circ$  in both tubes with the following results: tube 1,  $T = 28.94$ ; tube 2,  $T = 28.88$ ; and the value for the surface tension of water at the same temperature was found to be 72.62. The results generally are higher than those obtained by other observers using the capillary tube method, as might be expected owing to the use of the wider tubes.

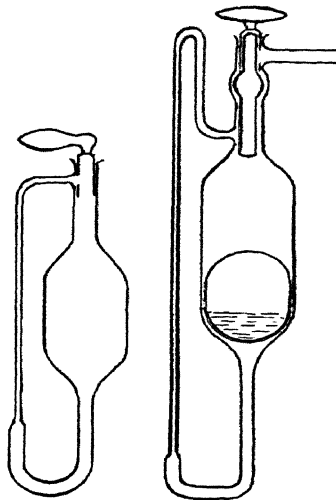


FIG. 28 (XII)

**Manometric Method.** A very convenient modification of the capillary-tube method has been used by Ferguson and Dowson.<sup>1</sup> The pressure required to force the meniscus back to the mouth of the capillary tube is measured. A diagram of the apparatus is appended. The pressure is produced by gently raising or lowering the bottle on left. This may be

done by means of a rack and pinion, and the corresponding pressure is read off on the manometer (Fig. 29 (XII)).

The original experimenters used a paraffin of specific gravity 0.856 at 15° in the manometer. The reading of the manometer is taken by means of a cathetometer. The capillary is cleaned with the usual liquids and dried with filtered hot air. It is then fused on to the wide tube just below the stopcock. After any one determination the capillary may be cut off, cleaned, and dried before using again.

The vessel containing the liquid, the surface tension of which is required, is placed on a movable table, and raised until the surface of the liquid just

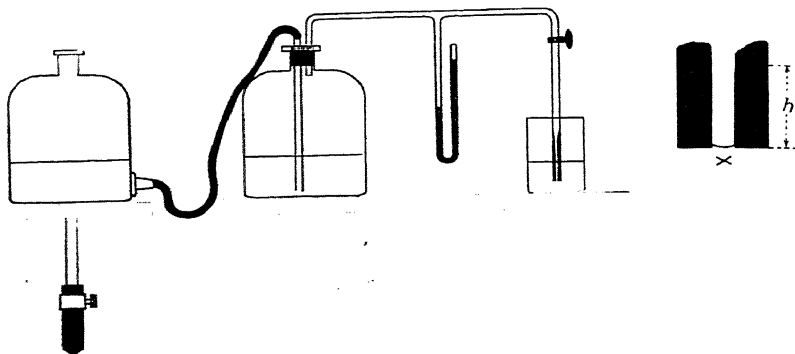


FIG. 29 (XII)

comes into contact with a pointed index, firmly fastened to the capillary at a distance  $h$  from the end of the tube.

By gently raising the bottle on the left the surface of the liquid is gently forced down until the lowest point in the capillary surface (viewed through a low-power microscope) is on a level with the bottom of the capillary tube. The reading of the manometer is then taken. The value may be verified by taking readings when the meniscus is just within and just without the capillary. The mean of these also gives the 'crucial' pressure. The diameter of the capillary tube at the end may be determined by the optical method. An average of a large number of readings must be taken. The interfacial tension may then be calculated, using the formula

$$T = g \frac{r}{2} (\rho_1 h_1 - \rho h) + \frac{g \rho r^2}{6}$$

where  $r$  = radius of capillary

$h$  = distance from index to end of tube

$h_1$  = liquid head in manometer

$\rho$  = density of experimental liquid

$\rho_1$  = density of liquid in manometer

The method is convenient and has a number of very obvious advantages, of which the following are the more important:

- (1) Capillary calibration troubles are completely avoided. Bore at the end only is measured.

- (2) Capillary is quite short and more easily cleaned and kept clean.
- (3) Thermostatic arrangements are convenient.
- (4) The cathetometer measurement of the pressure is much simpler than of the capillary rise.

The sensitiveness of the apparatus depends on the fineness of the mechanism used for raising and lowering the head of water.

**Drop Method.** Tate made experiments upon the weight of a drop of water falling from the end of a glass tube. He used tubes from 3 to 17 mm. in diameter and made of thin glass ground to a sharp edge. He came to the conclusion that the weight of the drop is proportional to (1) the diameter of the tube; (2) the weight of the liquid which would be raised up in the tube owing to the capillary; and he found that the weight decreased with rise of temperature. His first two conclusions may be stated in the form  $mg = k.rT$ .

Many text-books and research workers describe methods using capillary tubes without any reference to the sharp edges, and using the equation  $mg = 2\pi rT$ , i.e. making Tate's constant  $k$  equal to  $2\pi$ . Poynting and Thomson (*Properties of Matter*) point out that the forces acting on the drop include the excess pressure over the external pressure which is developed in the drop owing to surface tension; if the drop is cylindrical at the top, the value of this excess pressure is  $T/r$ , and we then have  $2\pi rT = mg + \pi rT$ —i.e.  $mg = \pi rT$ , or exactly half the previous value. Rayleigh finds that that the equation  $mg = 3.8rT$  is sufficiently accurate for most purposes, while J. L. R. Morgan finds  $mg = 3.94rT$ . There is thus some doubt as to the exact value of the constant to be used, but this difficulty is overcome by Morgan and co-workers<sup>1</sup> by using the falling-drop method to give values of the surface tension relative to that of benzene as determined by the capillary-rise method. As a general method Morgan's has the advantage over the capillary-rise method that the surface of the drop is a large one, and moreover is constantly renewed, so that the effect of small quantities of impurities is much reduced. Morgan's apparatus can be used for all temperatures up to 90°, and errors due to evaporation are avoided. He has established from a long series of experiments that for a given dropping tip the ratio of the surface tension to the weight of the falling drop at the same temperature is equal to a constant, i.e.

$$\frac{T_{C_6H_6,t}}{mg_{C_6H_6,t}} = \frac{T_{H_2O,t'}}{mg_{H_2O,t'}} = \frac{T_{I,t''}}{mg_{I,t''}} = C$$

wherefore  $T_{I,t''} = Cmg_{I,t''}$  for any given tip. Each tip has to be standardized by means of benzene or water, using the values

$$\begin{aligned} T_{C_6H_6,t} &= 30.514 - 0.1321t + 0.000082t^2 \\ T_{H_2O,t} &= 75.872 - 0.154t - 0.00022t^2 \end{aligned}$$

The equation for benzene is derived from the average of all the results of all accurate workers using the capillary-rise method; that for water was obtained by comparison with benzene using the drop method.

The laboratory form of Morgan's apparatus is made entirely of glass,

<sup>1</sup> *J. Amer. Chem. Soc.*, 1908, 30, 360, 1055; 1911, 33, 349, 643, etc.; 1913, 35, 1249, 1750, 1505, 1821. See above, page 89.



the various parts fitting together by means of ground-glass joints (Fig. 30 (XII)). It consists essentially of two stoppered straightsided weighing bottles 2 cm. diameter connected by an inverted capillary U-tube, one limb being slightly shorter (1 cm.) than the other. The weighing bottles, by means of their stopper, fit into a perforated disc, which in its turn fits into a larger weighing bottle, the latter serving as an air bath. The two

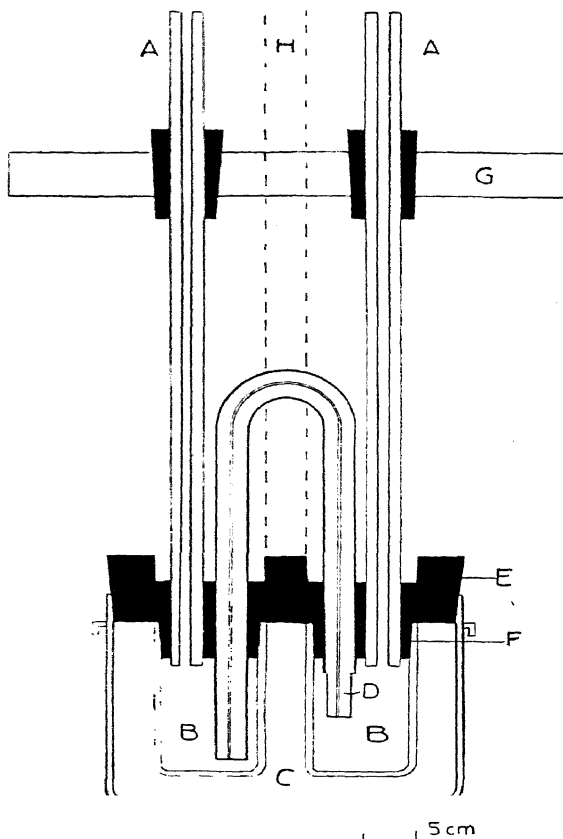


FIG. 30 (XII)

weighing bottles and the outer air-bath are all supplied with ventilation tubes, and a thermometer is attached having its bulb close to the U-tube. The inverted tube is the 'capillary'-drop tube, and has the shorter end ground accurately cylindrical for a length of 1 cm. to take the tip; the bore of this tube is 0.2 mm. Tips of various sizes can be fitted; the bottom of the tip is made plane and perpendicular to the sides, a clean sharp edge being very important. When the apparatus is fitted with a fresh tip,

great care should be taken to get the bottom of the tip exactly parallel to the cover of the apparatus, so that the tip can afterwards be set exactly level by levelling the cover. Before using, the apparatus is very thoroughly cleaned with the usual liquids. A rubber bulb is connected to the ventilation tube, which fits into the weighing bottle on the tip side; the compression of the bulb can be controlled accurately by means of a screw. The empty weighing bottle on the tip side is put on first, and then that containing the liquid is fitted in position on the supply side, and the outer vessel is attached; the whole apparatus is placed in the thermostat and allowed to remain for 20 to 40 minutes to attain thermal equilibrium, the capillary being kept free from liquid the whole time by means of the compression bulb. The tip is then carefully levelled by getting the cover of the apparatus level (parallelism between the two having been carefully attended to in the original assembling of the parts). The liquid is now sucked slowly through the capillary, and a drop of nearly the maximum size is allowed to form; this drop is left hanging for 5 minutes so that any evaporation effects which are going to occur may be completed; the drop is then allowed to fall and 29 other drops are collected, each being allowed about one minute to form, and its shape being observed during its formation by means of a lens to ensure that the drops are 'normal', great care being taken that the drops fall of their own weight, by making the rate of formation very slow towards the end of the formation of each drop. The liquid in the capillary is then forced back, and the weighing bottle on the supply side is removed; any liquid adhering to the capillary is taken up with filter-paper. The weighing bottle on the tip side is dipped in cold water to condense any vapour, and the outside having been dried, the bottle is disconnected, stoppered and weighed. The weight so obtained is that of a bottle together with thirty drops of liquid and a certain amount of vapour. The weighing bottle on the tip side is dried, and the parts of the apparatus are assembled in the same order as before, and the whole part is placed in the thermostat and left for the same time as in the first part of the experiment; a single drop is formed and allowed to hang for five minutes; five drops are then allowed to fall, and the sixth is kept hanging at the end of the tip until the total time is the same as in the first experiment; the sixth drop is then forced back into the supply vessel, and the weighing bottle containing the five drops is removed with the same precautions as at first and is weighed. This gives the weight of the bottle together with five drops and a certain amount of vapour, which, owing to the conditions of the experiment, cannot be very different from that in the first experiment. Thus, if the second weight is subtracted from the first, the weight of twenty-five drops is obtained.

Morgan's drop-weight apparatus is made by Eimer and Amend of New York.

**Drop Weight Method.** The *drop-weight*, as distinct from the *drop-number* method for the measurement of surface-tension, is, according to Ferguson,<sup>1</sup> a method capable of results of very high precision. It is not an absolute method, inasmuch as the final calculation of the surface tension is made from data taken from a curve drawn as the result of experiments on the drop-weights of a series of standard liquids.

<sup>1</sup> *J. Sci. Inst.*, 1929, 6, No. 5.

One of the essential conditions for the success of the drop-weight method is that the drop shall be formed, at least in the stages immediately preceding its detachment, with great slowness. Abonnenc<sup>1</sup> finds that the mass ( $m$ ) of a detached drop is connected with the number ( $n$ ) of drops falling per second by a relation of the form

$$m = a + bn - cn^2$$

and Harkins and Brown<sup>2</sup> quote the figures following for the relation between weight and time of free formation of a water drop detached from a given tip :

Time		Weight
min.	sec.	(gm.)
1	20	0.07191
1	45	0.07187
3	30	0.07179
6	00	0.07172
9	00	0.07174
10	00	0.07175

About 4 minutes is the minimum time that can be allowed for drop formation in this particular instance.

In the practice of the drop-number method, instead of directly determining the weight of a single drop, the number of drops formed by a given volume of liquid is determined.

The simple apparatus for the measurement of interfacial tensions between oil and acid described by Edwards<sup>3</sup> substitutes an automatic counter for the human observer. In his instrument the falling drop bridges a gap in an electrical circuit and thereby operates a relay which governs an automatic counting device. In this form, it is presupposed that one liquid is conducting and one non-conducting, but there seems<sup>4</sup> to be no reason why the mechanical force of the falling drop should not be utilized to close the relay circuit temporarily, thus enabling experiments to be carried out with certain of the non-conducting liquids whose interfacial tensions have been studied by other and independent methods.

**Method of Jaeger.** A method depending on the formation of bubbles of air in the liquid is that described by Jaeger. The pressure inside a spherical air-bubble in a liquid exceeds that outside by an amount  $p$  given by the equation  $p = 2T/r$ ; at constant temperature the product  $pr$  is constant. Now, if a glass tube is placed vertically in the liquid, and is attached to an air vessel fitted with a manometer, on gradually increasing the pressure, the air will pass down the tube and a bubble will form at the end. If the pressure is then slightly increased, since  $pr$  is to remain constant, the radius of curvature of the drop must diminish as the volume of the drop increases; the drop thus continues to grow until it becomes hemispherical. The excess pressure  $P$  above that of the atmosphere shown by the manometer is then equal to the hydrostatic pressure plus the pressure due to the curvature of the drop, i.e.

$$P = dgh + 2T/r$$

<sup>1</sup> *Compt. rend.*, 1917, 164, 402; 1919, 168, 556.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1919, 41, 499.

<sup>3</sup> *J. Sci. Inst.*, 1929, 6, 90.

<sup>4</sup> Ferguson, *J. Sci. Inst.*, 1929, *ibid.*

where  $d$  is the density of the liquid

$h$  is the depth of the end of the tube below the surface

$T$  is the surface tension

and  $r$  is the radius of the tube (see Fig. 29 (XII) )

If the pressure is again slightly raised, since the radius of curvature of the drop cannot be less than the radius of the tube, the radius of the drop must increase as the volume increases and the capillary counter-pressure is reduced ( $pr$  being fixed); thus, a very slight increase in the pressure above the value given in the equation causes the drop to continue to increase in size until it detaches itself. The experiment therefore consists in finding the minimum pressure at which bubbles will continue to form and detach themselves from the tube. Capillary tubes having very sharp edges are used, and two tubes of different radii are attached to vertical rods so that they can be moved up and down a vertical scale. The two tubes are attached to the same air reservoir, and the heights are adjusted until bubbles slowly detach themselves from both tubes simultaneously; then

$$T = \frac{rr'g}{r' - r} \cdot dh$$

and the actual value of the pressure is not required. Since

$$T'/T'' = d'h'/d''h''$$

the method is very convenient for determining relative surface tensions.

Harkins and Brown<sup>1</sup> have indicated that an error in results by methods involving buoyancy of a bubble of gas in a liquid is caused by lack of sharpness or departure from the circular shape of the tip. Errors become more important as the tip decreases. An error of 0.005 mm. in the radius of a 1 mm. tip causes a discrepancy in the surface tension of 0.5 per cent.

Jaeger's method is also much used for absolute measurements. The results are completely independent of the existence of a contact angle and the method admits of very accurate temperature control. It is obviously an ideal one for the determination of liquid and gas interfacial tensions. Ferguson has used it to determine the difference in the tensions of water in contact with air and carbon dioxide. The capillary is connected to a T-piece, one side going to the manometer and the other to the single arm of a Y-tube. The other arms are connected to an air-pressure bottle and a carbon dioxide generator. The flow is in each case regulated to give bubbles every two or three seconds and the extreme pressure measured. The tension is calculated from the exact formula

$$\frac{T}{g\varrho'} = B + \frac{r^3\sqrt{3}}{12B}$$

and

$$B = \frac{r}{g\varrho'} \left\{ \varrho_1 h_1 - \varrho' \left( h' + r - \frac{r}{3} \right) \right\}$$

$\varrho'$  = density of experimental liquid

$r$  = radius of capillary

$\varrho_1$  = density of liquid in manometer

$h_1$  = pressure in manometer

$h'$  = depth of capillary below surface

<sup>1</sup> *J. Amer. Chem. Soc.*, 1919, **41**, 523.

The latter measurement is obtained by fixing a needle to the side of the tube and just allowing its point to touch the liquid surface. The distance from the point of the needle to the end of the tube is then measured with a cathetometer.

**Sentis' Method.** A very ingenious method, suitable when only small quantities of liquid are procurable, is that due to Sentis. This method requires the measurement of the radius of a drop pendent from a capillary tube. The liquid is drawn into the capillary tube and allowed to flow out; a pendent drop is thus formed at the end of the tube, the latter being vertical (Fig. 31 (XII)). The maximum diameter of the drop is measured by means of a travelling microscope. The distance from the lowest point of the drop to the level of the meniscus in the tube is also measured and the position of the latter marked. A beaker containing the liquid is then placed underneath the drop on a movable table and raised until the drop is absorbed in the liquid and the meniscus in the tube restored to its former level. The distance from the meniscus to the level of the liquid in the beaker is then measured ( $h_2$ ). The tension is then calculated from the formula

$$T = \frac{g\rho}{2} \left\{ r \{ h_1 - h_2 \} - \frac{r^2}{3} \right\}$$

where  $\rho$  = density of the liquid

$r$  = maximum radius of drop

$h_1$  and  $h_2$  = the length measurements

As the difference ( $h_1 - h_2$ ) only is required in the formula, the two may be combined in one measurement. The beaker containing the liquid is placed on a spherometer table and raised until the liquid surface just touches the bottom of the drop. The further distance to restore the meniscus to its original position is then directly measured. This method is capable of a high degree of exactness and it is independent of the angle of contact; the only objection to it is the difficulty in registering the temperature of the drop.

**Torsion Balance.** For the rapid determination of the surface tension of small quantities of liquid (1 ml.) the method of Lecomte du Noüy<sup>1</sup> may be employed. The method is very advantageous where quick measurements are desirable, as when the surface tension is varying rapidly. The method is based upon the adherence of a platinum-iridium ring to the surface of the liquid. The torsion of a wire is used to counteract the tension and break the film between the ring and the liquid.

The instrument (Fig. 32 (XII)) consists essentially of a stand provided at the top with a fine steel wire stretched between end supports. One end of the wire is tightly clamped, the other being attached to a worm-wheel controlled by a thumb-screw. To the worm-wheel is also attached a pointer which moves over a circular scale graduated in degrees. To the middle of the wire is clamped a hollow, light aluminium lever with a small hook

<sup>1</sup> *J. Gen. Physiol.*, 1918, 1, 521; 1923, 5, 429.

in the outer end. A stirrup attached to this hook carries a carefully made hoop of platinum-iridium wire with a periphery exactly 4 cm. in length. The watch-glass or other vessel containing the liquid whose surface tension is to be determined is placed on the platform, which can be raised carefully by an adjusting screw until the platinum loop makes contact with the liquid.

The pointer having been previously set at zero, the tension of the wire

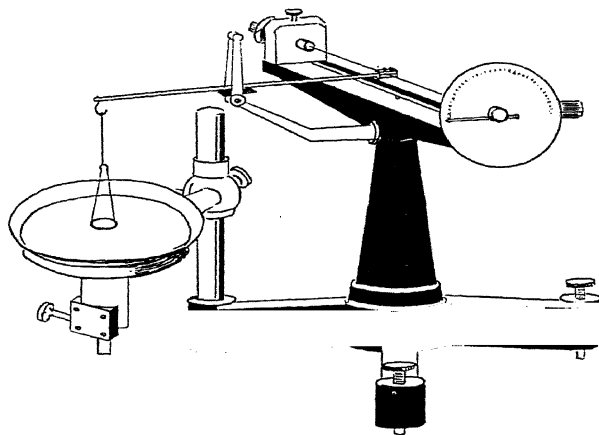


FIG. 32 (XII)

is gradually increased by means of the thumb-screw controlling the worm-gear, until the loop of wire tears free from the liquid. The number of degrees is then read on the scale. To make an absolute measurement a piece of paper is now cut to fit over the platinum ring. On top of this paper weights are added till the pointer is brought back to its zero position. Then  $M$  = mass of (weights added + weight of paper) must be the pull of the liquid surface of the ring in grams-weight.

If  $L$  is the circumference of the platinum ring, then

$$T = \frac{Mg}{2L}$$

since there are two surfaces to the film.

Once a standard measurement is made with the instrument the surface tension of all other liquids may be obtained from their angle of torsion by direct proportion.

With this instrument a determination takes from 15 to 30 seconds and 1 ml. of liquid is sufficient, and the results are reproducible within very narrow limits.

A convenient method has been devised by Sutton<sup>1</sup> for measuring simultaneously the surface tension and the density of a sample of liquid. A few milligrams of liquid will suffice. The method has advantages, therefore,

<sup>1</sup> *Proc. Phys. Soc.*, 1933, 45, 88; see also *Proc. Phys. Soc.*, 1934, 46, 510; *J. Phys. Chem.*, 1934, 38, 6, 779; Ferguson and Kennedy, *Proc. Phys. Soc.*, 1932, 44, 511; Sugden, *J. Chem. Soc.*, 1924, 125, 27; Mahajan, *J. Sci. Inst.*, 1936, 13, 189.

for the measurement of the parachors,  $\gamma^{\frac{1}{2}}/\rho$ , of rare liquids. Volatile liquids may be used.

Two tubes, differing in size of bore, are fused together. The liquid is then introduced so as to lie across the join and extend into the uniform portions of the tube. The tendency is for the liquid to pass into the tube of finer bore. If, however, the system is held vertically with the finer bore uppermost, this tendency is balanced by the weight of the column of liquid. A steady state is attained when <sup>1</sup>

$$\frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'} = \rho gh$$

where  $\gamma$  is the surface tension,  $r$ ,  $r'$  the radii,  $\rho$  the density and  $h$  the height of the column. If the dimensions of the tube are known this is sufficient to determine the surface tension in terms of the density. In practice, however, it is more convenient to connect the end of the tube to a gas-reservoir fitted to a manometer, and to proceed as follows.

Adjust the pressure in the reservoir so as to bring the meniscus to a chosen marked position L in the finer bore. A state of stable equilibrium is attained when

$$\left( \frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'} \right) - \rho gl = p_1 \quad (1)$$

where  $l$  is the vertical distance between the ends of the column of liquid and  $p_1$  is the pressure recorded on the manometer.

The tube is then inverted so that the finer bore is now in the lower end. In this position the capillary forces and the weight of the column both tend to draw the liquid downward. Equilibrium is attained when

$$\left( \frac{\gamma}{2\pi r} - \frac{\gamma}{2\pi r'} \right) + \rho gl = p_2 \quad (2)$$

where  $p_2$  is the pressure recorded on the manometer when the tube has been inverted in this way.

This equilibrium, however, is unstable and the meniscus is brought to the chosen position by adjusting the pressure in the reservoir successively above and below  $p_2$ . Provided the finer bore is such that the viscous resistance of the liquid makes the movements within the tube appropriately slow, this measurement can be made with considerable precision.

To standardize the tube, a value is required for  $(1/2\pi r - 1/2\pi r')$ . This may be obtained by measuring the stable equilibrium given by relation (1) with a standard liquid in the tube. In most instances water or benzene may be used. By this means

$$\left( \frac{1}{2\pi r} - \frac{1}{2\pi r'} \right) = \frac{p' + \rho_s gl'}{\gamma_{(\text{standard})}} = \frac{1}{k}, \text{ say}$$

where  $\rho_s$  is the density of the standard liquid, and  $p'$ ,  $l'$  are the corresponding values obtained for  $p_1$  and  $l$ .

<sup>1</sup> If the liquid makes a contact angle  $\alpha$  with the tube,  $\gamma$  should be replaced by  $\gamma \cos \alpha$  throughout the equations.

The relations (1) and (2) may now be written in the convenient form :

$$\gamma = \frac{1}{2}k(p_1 + p_2) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

$$\rho = (p_2 - p_1)/2gl \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

To compare the surface tensions of two liquids (3) may be written :

$$\frac{\gamma}{\gamma'} = \frac{p_1 + p_2}{p_1' + p_2'} \quad (5)$$

where  $\gamma'$ ,  $p_1'$  and  $p_2'$  refer to the second liquid.

In this relation the dimensions of the capillary tubes have been eliminated, so that the measurements depend entirely on readings of the manometer attached to the gas-reservoir. The accuracy of the method depends therefore on (i) ensuring that the volume of liquid is constant and that the liquid is brought to the standard mark L, and (ii) employing a sensitive and reliable manometer. When the liquid is scarce Fig. 33 (XII)*a* may be used. If the liquid is limpid as well as scarce, the necessary resistance to motion is obtained by choosing tubes of fine bore. If more liquid is available, it may be found more convenient to obtain this resistance by bending a tube of somewhat coarser bore into the form (Fig. 33 (XII)*b*).

In either case, it is desirable that the tube should be provided with a means of obtaining a sample of standard volume. This is effected by making the finer tube somewhat longer than would otherwise be necessary, and blowing a small bulb about 1 cm. from the end (see diagram). If the liquid is now drawn into the tube to the fixed mark M, a fixed volume is obtained, which may subsequently be made to fill the equal volume bounded by the marks L and L'. Long tubes have the further advantage that evaporation is reduced to a minimum. The measured value of the surface tension under these conditions is that of the liquid in contact with an atmosphere saturated with its own vapour.

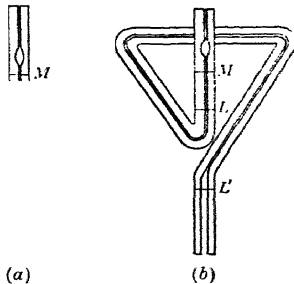


FIG. 33 (XII)

An improved precision torsionmeter of the du Nöy form made by the Central Scientific Company of New York has a fine steel torsion wire, secured at both ends in torsion heads each of which is driven by a worm-gear arrangement which permits very precise adjustment. The forward tension head extends through the scale and carries a vernier which permits a reading of the scale directly to 0.1 dynes and estimation to 0.05 dynes. The scale, which is engraved on a 4-inch dial of nickel silver, has a range from 0 to 100. The torsion head is mounted on ball bearings.

The zero-balance position of the lever arm carrying the ring is indicated by a sharp pointed index, attached to the lever arm, against an engraved line on a small plane mirror mounted on the bracket. The zero-balance may be adjusted to within 0.02 mm. by this means. The ring and supporting stirrup are made of platinum-iridium wire with all joints welded. This ring is supported on the end of a light arm consisting of a steel tube having a length of approximately 10 cm. The clamp which secures the arm



to the torsion wire is so constructed that an adjustment of 5 mm. in the effective length of the arm can be made. This permits the scale of the instrument to be standardized to become direct reading in dynes per centimetre for subsequent measurements.

Freud and Freud<sup>1</sup> and Harkins and Jordan<sup>2</sup> showed that a correction factor  $F$  is necessary in the expression for the surface tension which now becomes

$$T = \frac{Mg}{2L} \times F$$

The value of the correction factor may vary, in extreme cases, from unity by as much as  $\pm 30$  per cent. The value for the 4-cm. ring used with the instrument described above, employed in pure water at room temperature is approximately 0.990 and for the 6-cm. rings 0.940. The factor is a function of  $R/r$  and  $R^3/V$  where

$R$  = the mean radius of the ring in centimetres

$r$  = the radius of the wire of the ring in centimetres

$V$  = the maximum volume of liquid raised above the free surface of the liquid

The method of determining the factor is described in the papers quoted.

*The Importance of Extreme Cleanliness* is emphasized by du Noüy. He says: 'Errors introduced in measurements through the use of glasses, pipettes and funnels which have been insufficiently cleaned or cleaned with alcohol or ether, can, in certain cases, amount to 30 per cent, while all other causes put together do not amount to 5 per cent . . . It is therefore of fundamental importance to conform rigorously to the following indications, which are the result of several years' experience, if it be desired to obtain constant results or at least to eliminate the most prolific source of error. All glassware must be boiled, for two hours at least, in a solution of 10 to 15 per cent potassium chromate in concentrated sulphuric acid. The liquid must be frequently stirred and the objects moved around one by one with forceps, in order to make sure that small air bubbles do not protect any part of their surface. As to graduates, test tubes, &c., the liquid at the bottom must be frequently changed by means of a glass tube with a rubber bulb attached by which the liquid is aspirated. For pipettes it is sufficient to adjust a rubber tube at one of the extremities and to produce by suction a rapid and frequent alternative movement of the liquid. The standard volumetric flasks must be filled with cleaning solution which is kept at the boiling-point for 2 hours, after which the liquid is allowed to cool for 12 hours during which it should be shaken vigorously at least three or four times. The objects are then rinsed under a jet of distilled water. If the vessel containing the distilled water be of glass it must naturally have been subjected to the same process. The rinsing by running distilled water must be thorough. The different pieces are then allowed to dry in a place where they are protected from dust, in an incubator, for example, on clean filter paper.'

The large temperature coefficient of surface tension is well known and in order to keep the temperature constant during measurements it is advis-

<sup>1</sup> *J. Amer. Chem. Soc.*, 1930, 52, 1722.

<sup>2</sup> *Ibid.*, 1751.

able to have the liquid at a temperature close to that of the room and to keep it covered to prevent loss of heat by evaporation. Covering the liquid also helps to keep it from contamination from the air. One method is to place the vessel containing the liquid in a larger one which can be covered by two pieces of cardboard notched so that they may overlap slightly without touching the wire. The platinum ring should be heated to a bright red in a bunsen flame just before a reading is taken since a lapse of only 30 seconds results in a lower reading.

**Interfacial Tension.** Most of the methods described above can be modified to the measurement of liquid—liquid interfacial tension. Absolute measurements of interfacial tension are not very often made, comparative values being more commonly needed. For absolute measurements the capillary-rise method and a modified drop-weight method have been used.<sup>1</sup> To obtain complete details of these methods the original papers should be consulted. The capillary-rise method is applied by fixing the capillary so that it may be raised and lowered in the more dense liquid. This is placed in a wide tube. The capillary is fixed vertically and completely submerged. The lighter liquid, which must be immiscible and non-reactive with the more dense, is then poured on top. The capillary is raised into the lighter liquid and the height of the meniscus in the capillary above the surface of the heavy liquid is measured.

The theory of the drop-weight method is as before, but now interfacial tension and apparent weight are the factors. The essential feature in the drop-weight apparatus is the tip of the dropping pipette. The tip must be ground almost perfectly round, with very sharp edges. For dropping water into other liquids the optimum diameter for the tip has been determined as 9.5 mm. The apparatus consists of a pipette B of capacity 10 ml. (Fig. 34 (XII)). Above and below the bulb the stem is graduated to 0.1 ml. so that readings may be made to 0.01 ml. To give better control of the drop the long vertical capillary tube C-D has a diameter as small as 0.3 mm. The short arm H at the right which has the tip at its lower end is sealed into a large glass stopper E. The glass beaker which holds the lighter liquid is fastened to the glass stopper by means of a ground joint. A spirit level is fixed to the instrument to set the tip horizontal. The pipette is filled by suction at A to the 0.2 or 0.3 mark on the stem above the bulb, and the liquid allowed to run out to 0.0 mark. The lighter liquid is placed in the beaker and raised till its surface is about 1 cm. above the tip.

The apparatus is then allowed to attain a constant temperature in a thermostat. After half an hour the tube G is connected to a suction pump and the suction regulated so that drops come every three minutes. The number of drops to exhaust a certain volume is then counted. The densities of the two liquids are determined with a pycnometer and the apparent weight of the drop calculated.

Absolute measurements are not often needed in physico-chemical problems; approximate comparative values usually are sufficient. For these determinations a simple modification of the drop-weight apparatus, such as Donnan's, may be used.

<sup>1</sup> Harkins and Humphrey, *J. Amer. Chem. Soc.*, 1916, 38, 236.

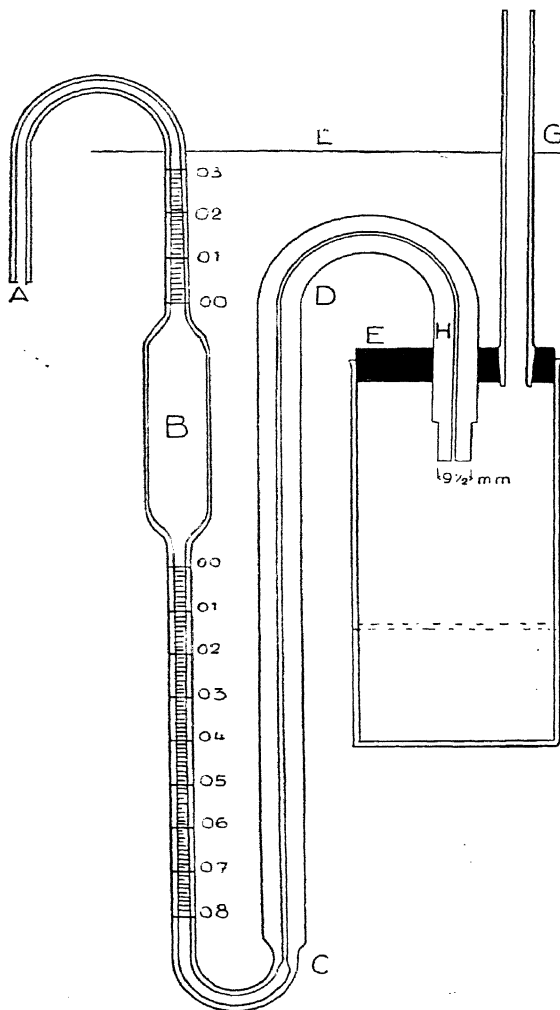


FIG. 34 (XII)

**Drop Pipette** (Fig. 35 (XII)). The Donnan pipette<sup>1</sup> consists of a tap at *b* (not shown), a bulb *c* of about 5 ml. capacity, a capillary tube at *q* (N.B. inner bore of capillary tube not shown, it extends nearly to base of tube), and a wider tube drawn out into a point at *d* which is ground flat as at *e*. The pipette is filled with a liquid such as petroleum ether to the top mark *f* and immersed with its point below the level of the liquid to be

<sup>1</sup> See *The Donnan Equilibria*. Bolam. (G. Bell, London.) 1932.

tested. The tap is then opened and the number of drops formed by the petroleum ether in running out to a lower mark on  $q$  is noted. This number is fixed by the difference in the specific gravity of the two liquids, which must be immiscible with one another, and by the surface tension acting around the drop. A diminution of surface tension tends to increase the number of drops. By varying one liquid and keeping the other constant the surface tensions of a number of liquids may be compared.

The drop pipette method has also been employed to measure the adsorption effects at liquid-liquid interfaces (surface of separation of a hydrocarbon oil and an aqueous solution of sodium glycocholate). It has also been applied to obtain the acidity of solutions by determining the number of drops formed by the flow of a given volume of standard alkali from a drop pipette immersed in a given volume of the acid solution. By varying the volume of alkali run in, the number of drops shows a sudden increase at the neutralization point.

For the determination of molecular surface energy of water and the association factor, see Rae and Reilly, *Physico-Chemical Practical Exercises*, Methuen & Co., 1934.

#### Du Noüy Interfacial Tensiometer.

Interfacial tensions between certain liquids, such as water and a liquid lighter than water, may be made with an upward pull on the ring in the du Noüy instruments already described; but for a great many liquids the instruments are not suitable. In numerous cases it becomes necessary to measure downward forces as well as upward forces.

The interfacial instrument carries the ring on one vertical limb of an articulated parallelogram, one corner of which is clamped to the torsion wire. The other three corners have delicate pivot and jewel bearings. The horizontal limbs are independently adjustable in length by means of finely threaded screws, the knurled adjusting heads of which are marked so that equal adjustments may be made accurately on both. This adjustment makes possible a direct reading scale in dynes per centimetre. The parallelogram may be clamped during the removal or replacement of the ring. The graduated dial reads in both directions from the zero and a double vernier is provided. A 6 cm. ring is used and readings may be made to 0.1 dynes.

**Measurement of Surface Tension by Breaking of a Film.** When a drop of olive oil or castor oil is placed on a large clean surface of water, the oil spreads rapidly and covers a definite area. Rayleigh measured the surface tension of the contaminated water by Wilhelmy's method. That is, a thin blade was mounted in a balance, its plane being vertical and its

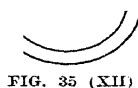
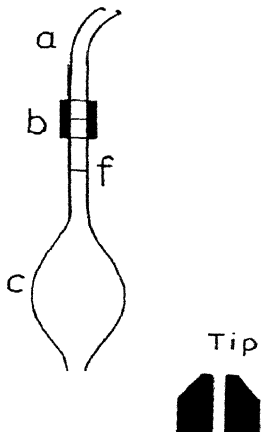


FIG. 35 (XII)

SURFACE TENSIONS OF SOME COMMON LIQUIDS IN PRESENCE OF THEIR  
OWN VAPOUR IN DYNES PER CENTIMETRE

Liquid	Temperature, °C.	Surface tension against own Vapour
Alcohol ethyl	20	22.0
	40	20.2
	60	18.4
	80	16.6
Alcohol methyl	20	23.02
	70	17.6
	100	14.8
Alcohol amyl . . .	20	24.0
Benzene . . . .	11.2	29.2
	46	24.7
	78	20.7
Chloroform . . .	10.2	27.6
	45.5	23.0
	77.6	19.9
Carbon tetrachloride .	20	25.7
	80	18.7
Ether . . . . .	20	16.5
	30	15.3
Ethyl acetate . . .	20	23.6
	80	16.3
	100	13.4
Ethyl formate . . .	10	24.2
	46.5	19.6
	80	15.5
Glycol . . . . .	16.8	46.4
	46.1	43.9
	78.2	40.8
	131.9	35.3
Mercury . . . . .	15	45.3
Nitric acid . . . .	15	42.0
Pyridine . . . . .	17.5	36.7
	56.3	30.9
	78.6	28.5
	91.0	26.5
Sulphuric acid . . .	15	62.0
Water . . . . .	0	73.2
	10	71.9
	20	70.6
	30	69.1
	40	67.5
	50	66.0
	60	64.3
	70	62.6
	80	60.8
	90	58.9
	100	57.2

lower horizontal edge dipping under the surface of the water. The oil was prevented from spreading irregularly by barriers consisting of strips of glass placed across the tray containing the oil and resting on the edges. As the 'thickness' of the oil film was varied by altering the barriers the surface tension changed. Devaux<sup>1</sup> developed a different method to study these films. A photographic tray is half filled with water and a little clear talc dusted on the surface. A strip of paper is then placed on the surface of the water and held by the thumbs against opposite sides of the tray. By pushing along this barrier all the oil contamination is pushed to the top of the plate, while the surface below is clean. This clean surface is now lightly dusted with talc. A fine wire is dipped into the water and the talc is immediately pushed back forming a circular area of apparently clear water. If only a small amount of oil is applied this circle increases. Devaux has determined the areas covered by monomolecular films from weighed amounts of oils. For details of this work, his original papers should be consulted.<sup>2</sup>

Langmuir has improved the procedure in the study of oil films to a great extent. In his method the difficulties in connection with contact angles and solid films are avoided and it affords a highly sensitive and accurate differential method of measuring slight changes in the surface tension of water. Fig. 36 (XII) shows a diagrammatic representation of the apparatus. The water is placed in an enamelled tray, T, which is about 60 cm. long by 15 cm. wide. Above the tray is arranged a small balance with knife edge, K. One end of the beam of the balance has a counter-weight, while the other has a small knife-edge from which hangs a pan, P. Two glass rods, R and R', cemented to the knife-edge, extend downwards and pass through two small holes in the strip of paper B which floats upon the surface of the water in the tray. To prevent the paper from being softened by the water, it may be prepared by dipping in a solution of paraffin and benzene. The strip B is about 5 mm. less than the width of the tray, so that it can move freely without touching the sides of the tray. The surface of the water between the strips A and B is covered by an oil film by placing one or two drops of a benzene solution of the oil on the water. As the strip A is moved forward the oil film advances and begins to exert a force on the strip B. It tends to make the oil film flow round the ends of the strip B. To prevent this, air jets are directed by the tubes, F F', against the surface. When the air jet is started, impurities on the surface, H, are blown away. The air

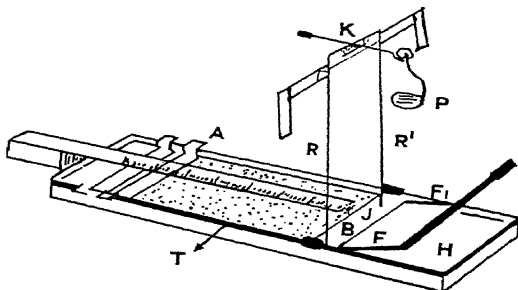


FIG. 36 (XII)

<sup>1</sup> See The Annual Report Smithsonian Inst., 1913, 261, for review of this work.

<sup>2</sup> *Soc. Franc. Phys.*, 1914, 35, 3; 57, 3, &c.

pressure on the balance is so adjusted that the centre of the edge of strip B is directly below the point J on the end of the meter stick.

A weight of 50 mg. is placed on the pan. This causes the rod R with the strip B to move until it strikes a stop not shown in the diagram. The strip A is placed on the surface and is moved along until it is close to the

strip B to test for residual contamination on the surface. When the edge of the strip is under the point J the force exercised by the oil film is the weight in the pan multiplied by the ratio of the arms of the balance (1 : 3). The distance from strip A to B is read off and in this way the residual contamination is determined. After cleaning two or three times the contamination can be reduced to less than 1 cm. with 50 mg. One or two drops of benzene solution are now placed on the surface between A and B and a 50 mg. weight placed in the pan.

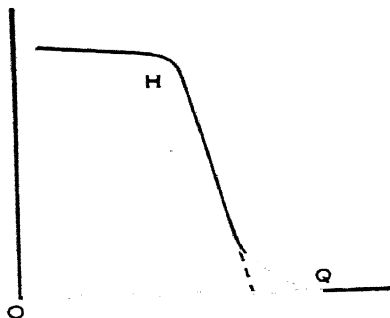


FIG. 37 (XII)

Strip A is moved until the oil film produces sufficient pressure against B to bring it under J. A reading on the meter stick is made. Then another 50 mg. is placed in pan and the strip A again moved until equilibrium is reached. Further weights are added until the oil film has been compressed into the space of a few millimetres. The force acting on the strip A is

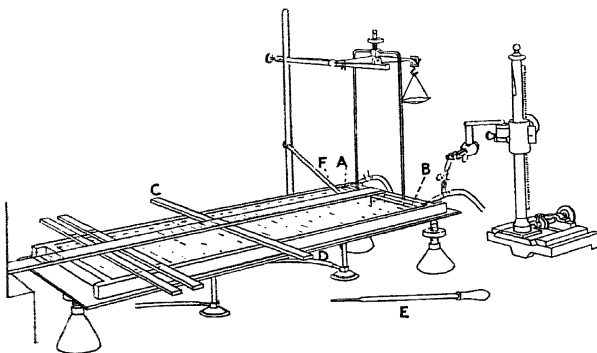


FIG. 38 (XII)

plotted as a function of the area included between the strips A and B. A typical curve is shown in Fig. 37 (XII).

The weights are plotted as ordinates and the distance between A and B as abscissae. When the area is greater than a certain definite limit Q, there is practically no force acting in the balance, but as the area decreases the force increases until it reaches a limiting value at the point H.

The instrument shown in Fig. 38 (XII) was devised by Adam<sup>1</sup>; it differs

<sup>1</sup> *Proc. Roy. Soc.*, 1922, 101, 454.

from Langmuir's in having a more satisfactory trough and it has barriers proof against leak. The trough is made of brass with thick barriers of rectangular section about 2 cm. wide and sufficiently heavy to remain in position. The surface is covered with hard paraffin wax to prevent leaking, and the tops of sides of the trough are similarly treated to prevent the water spreading so that no channels of liquid can form around the barriers. The floats extend around the whole trough except for about 1 mm. at each end. Leakage of the film past the ends of the float is prevented by air jets directed down against the narrow channels between the floats and the sides of the trough. This apparatus is suitable for surface tension as low as 0.5 dynes per centimetre. At lower pressure the air jet is strong enough to

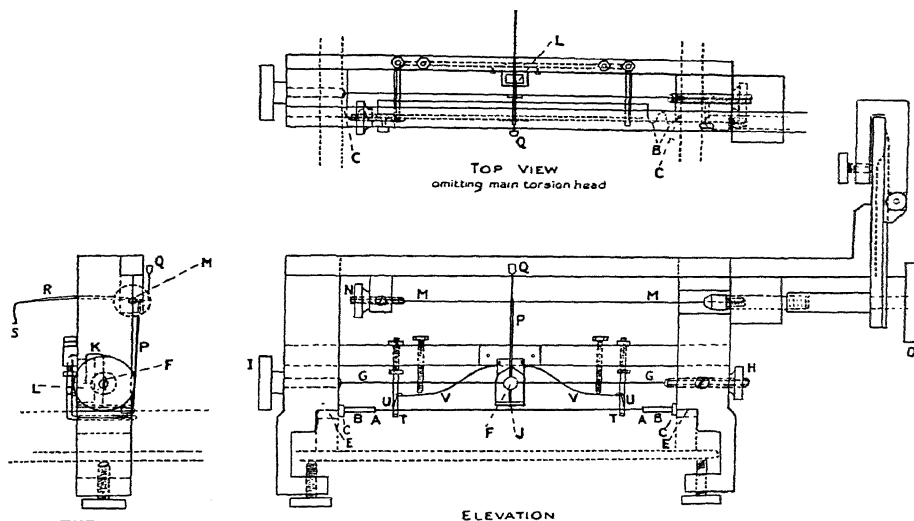


FIG. 39 (XII)

prevent leak may disturb the sensitivity of the balance. With the instrument shown in Fig. 39 (XII),<sup>1</sup> and also devised by Adam,<sup>2</sup> surface pressure as low as 0.01 dyne can be measured and accurate measurement of the critical angle can be made.

The trough, barriers and scale are similar to that used in the previous instrument. The float AA is of copper coil, 11 cm. long. The end carries small vertical strips of copper to which are soldered strips of gold ribbon, B (2 mm. wide and 0.009 mm. thick), fixed with the width perpendicular to the water surface. The other ends of the strips are soldered to brass pieces, CC, which form part of the frame of the machine. The mirror, F, indicating the position of the float, is carried on a very light holder on the torsion wire, GG, and connected to the float by a very fine silver wire. The measuring force required to balance the surface pressure of the film is applied to the float by a fine silver wire transmitting a tension forwards

<sup>1</sup> Made by Cambridge Inst. Co.

<sup>2</sup> *Proc. Roy. Soc.*, 1926, 110, 435.



from the lower end, P, of a rigid framework, which is fixed to a torsion wire on which the torsion can be varied and measured.

An apparatus for the same purpose is made by the Central Scientific Co. of New York. This 'Hydrophil' balance consists of an aluminium tray, 27 inches long by 6 inches wide, provided with levelling screws, drain cock and a movable barrier, to one end of which a bridge casting carrying a torsional device for measuring forces against a mica float, is mounted. The tray is accurately machined at the working edges to permit making accurate measurements of area: other portions of the tray are not machined to provide a surface to which a film will adhere. A metric scale is provided along one edge of the tray to indicate the distance of the movable barrier from the mica float. The torsional device consists of a suspension for the torsion wire, at one end of which a vernier pointer is attached for indicating the torsional force applied to the mica float on the circular graduated scale over which the vernier travels.

The use of the balance is described for measuring the percentage of hydrophils in lubricating oils.<sup>1</sup>

**Preparation of the Balance for Use.**—The scale is calibrated by suspending weights from 5 mg. to 500 mg. from a hook at the end of the lever arm and noting the number of degrees of counter torque necessary to restore the pointer to the zero point. The relationship between the counter torque caused by gravity acting on the weight used and the torque caused by the film pressure is calculated from the lengths of the respective lever arms between the weight and torsion wire and the torsion wire and the float. All parts of the apparatus which come in contact with an oil film during measurement must be coated with paraffin wax. The tray and barrier may be covered with molten paraffin which is smoothed out after hardening by gentle surface heating. The movable float and platinum ribbons are coated with paraffin by application as a solution in a volatile solvent such as benzene.

**Method of Measurement.** The paraffined tray should be filled with distilled water until the meniscus rises above the edge of the tray. The surface of the water on both sides of the paraffined float are swept free of contaminants by scraping the excess water away from the float by means of a straight edge. A film is formed between the movable barrier and the float, with the barrier initially placed near the end of the tray, by dropping a definite weight of oil upon the water surface. In most cases the oil to be investigated is weighed into a volatile solvent such as purified hexane or benzene. The concentration of this solution can be adjusted so that 1 ml. or less dropped from a graduated pipette will give a film covering at least one-half the area of the water surface. The solvent itself must not form a stable film, but serves the dual purpose of diluting the oil so that small quantities may be dispensed as relatively large volumes of solution and of diminishing the viscosity of the oil to the point where films form almost instantaneously and measurements may be begun as soon as the solvent evaporates.

The movable barrier is next carefully moved towards the float until a

<sup>1</sup> Langmuir, 'Mechanical Properties of Monomolecular Films', *J. Franklin Inst.*, 1934.

point is reached at which the film begins to exert a pressure against the float. The force is measured in degrees torsion necessary to bring the pointer back to the zero position. A record is taken of the positions of the movable barrier as it is moved towards the float and the corresponding forces exerted.

The data thus obtained are converted to dynes per centimetre (total forces divided by the number of centimetres active length of float, which includes the length of the mica plus half the width of the gaps occupied by the platinum floats) and areas in square centimetres. By plotting the forces as ordinates and areas as abscissae, a curve results which may be extrapolated to give the total film area under zero compression at the prevailing temperature.

**Computation.** The weight of oil involved in a measurement can be calculated from the volume of solution used. The molecular weight of the oil must be known or determined experimentally. By employing Avogadro's number,  $6.06 \times 10^{23}$ , the total number of molecules involved can be determined. Since only the oxidized molecules, or hydrophil groups, are responsible for the film, we can compute the number of these molecules present by dividing the total film area by the cross sectional area of the hydrophil group. For all practical purposes of comparison the cross sectional area of the stearic acid molecule, which has been accurately determined, may be used. This value is 22.3 square Ångström units. The percentage of oxidation products may also be calculated.

**Micro-Methods for Surface Tension Determination.** When only very small amounts of liquid are available for surface tension determination special methods may be employed for the test. Among these methods are the following, (a) Sugden's bubble-pressure method,<sup>1</sup> (b) Ferguson and Kennedy's<sup>2</sup> capillary method, and (c) Sutton's combined surface-tension and parachor method. This latter has already been described.

<sup>1</sup> *J. Chem. Soc.*, 1924, 125, 27.

<sup>2</sup> *Proc. Phys. Soc.*, 1932, 44, 551.

## SECTION 6: MONOMOLECULAR SURFACE FILMS <sup>1</sup>

Certain insoluble organic compounds (fatty substances, proteins, &c.) are capable of spreading out indefinitely on the surface of water even after they have been reduced to a layer a single molecule deep. A film already monomolecular in thickness cannot be made thinner, but the molecules may be separated more widely from each other, provided that a foreign substance which may happen to contaminate the surface does not hinder their expansion. By means of a method due to Devaux,<sup>2</sup> the region of a surface occupied by such a film may be rendered visible. The surface is lightly dusted with talc. If the surface is clean, and one blows tangentially to it, the particles of talc may be swept along and collected together at the walls of the containing vessel. If, on the other hand, the surface be contaminated, the talc grains may no longer be brought together. They adhere to the subjacent film, rotating under the action of the jet, but maintain unchanged their relative separations. Immediately the blowing is ceased the border of the talc-covered region will be seen slowly to invade the whole surface, the film expanding freely.

**Surface Concentration.** In studying this surface phenomenon the area occupied by the layer plays the same rôle as the volume in the equations of state of liquids or gases. In certain cases the surface concentration of a body is spoken of, that is the mass of the substance in question per square centimetre. When, however, the molecular weight is known, the term area per molecule is generally employed, and is expressed in square Ångström units ( $\text{\AA}^2$ ).<sup>3</sup> If the surface be limited to a certain size, the quantity of the fatty substance in the layer may be determined by preparing beforehand a solution of known concentration in benzine, or petroleum ether, and running a few drops of the solution on to the surface from a calibrated pipette or a micro-syringe. The solvent spreads, and then evaporates, leaving the fatty substance in the form of a film on the surface.

It is important to be able to increase or diminish at will the surface occupied by a known quantity of matter. To this end, certain workers use a rectangular frame made of four strips cut from thin mica and coated with paraffin (Fig. 40 (XII)). The mica so treated floats with its whole surface in contact with the water, the angle of contact between it and water being zero. Under these conditions such a frame forms an impermeable barrier to a film of oil which occupies the surface which it surrounds. Furthermore, a movable strip placed transversely and supported at each end by the frame may be used as a barrier to divide the surface into two compartments isolated from each other, the areas of which, however, are

<sup>1</sup> By Dr. D. G. Dervichian, Laboratoire de Chimie Physique, Paris.

<sup>2</sup> *Smithsonian Annual Report*, 1913, 261; *J. de Physique*, 1931, 7<sup>e</sup>, 2, 237.

<sup>3</sup> The Ångström Unit ( $\text{\AA}$ ) =  $10^{-8}$  cm.  $\text{\AA}^2$  =  $10^{-16}$  cm.<sup>2</sup>.

capable of being varied. Many workers use the edge of the trough itself to define the surface, in which case it must be kept at all times filled to the brim. In this case the surface is divided by a barrier consisting of a strip of paraffin-coated metal or glass resting on the edges of the trough which themselves must be treated with paraffin. The frame and moving barrier bear the same relation to films (two-dimensional fluids) as a cylinder and piston to liquids and gases (three-dimensional fluids).

**Cleaning of the Surfaces.** The first condition to be observed in the study of monomolecular films is that of scrupulous cleanness of the surface of the water. The technique described by Agnes Pockels<sup>1</sup> consists in sweeping the surface with strips which rest on the edges of the trough. Each strip gathers before it all the impurities and leaves behind it a fresh and clean surface. The following method may also be employed. The greater part of the impurities is removed by sweeping the surface with a sheet of thin paper which is applied to the water and swept back parallel to the surface. To complete the cleaning, the surface is dusted with talc. This renders visible the remaining impurities, which may then be concentrated by means of a jet of air into a corner, whence they may be removed through a tube drawn out to a point connected to a water jet pump.<sup>2</sup>

**Surface Pressure.** The presence of a film on water results in a lowering of the surface tension. If, therefore, the compartment A (Fig. 40 (XII)) be covered by a film, while the compartment B is clean, the surface tension ( $T$ ) in A will be less than that in B ( $T_0$ ), so that the barrier will be acted on by a linear pressure directed from A towards B equal to  $P = (T - T_0)$  expressed in dynes per centimetre length of the strip.<sup>3</sup> It may therefore be said that two-dimensional fluids exert a surface pressure which is a function of the surface occupied. Since  $P = T - T_0$ , variations in surface pressure may be studied by measuring the diminution in surface tension corresponding to each change in surface concentration (Rayleigh,<sup>4</sup> Agnes Pockels<sup>5</sup>). The pressure in the plane of the surface may be measured directly as has been done by Langmuir<sup>6</sup> (see last section).

This is achieved by dividing a surface into several compartments (Fig. 40 (XII)). The compartment A contains the film to be studied. By displacing the strip P the film may be extended or compressed. The force  $F$  necessary to maintain the free strip M in place position is measured. This force divided by the length of the strip gives the surface pressure per centimetre ( $P = \frac{F}{L}$ ). Langmuir was the first to employ a balance to measure this force  $F$ . The strip M

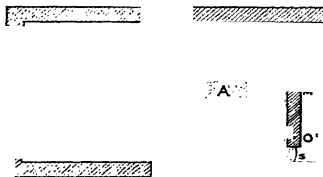


FIG. 40 (XII)

<sup>1</sup> *Nature*, 1890, 43, 437.<sup>2</sup> J. Guastalla, *Comp. rend.*, 1929, 189, 241.<sup>3</sup> In analogy with an ordinary pressure which is the force acting on a unit area.<sup>4</sup> *Phil. Mag.*, 1899, 48, 337.<sup>5</sup> *Ibid.*<sup>6</sup> *J. Amer. Chem. Soc.*, 1917, 39, 1868.

is joined rigidly to the axis of the beam of a balance, so that the horizontal displacements of the strip produce a rotation of the beam. The strip is restored to its original position by placing suitable weights in the pan.

A modification by Adam <sup>1</sup> of Langmuir's apparatus was shown in the section previous in Figs. 38 (XII) and 39 (XII). Marcelin <sup>2</sup> has used a torsion balance. Two vertical needle-like rods fit loosely into two holes near the ends of the strip, O and O' (Fig. 40 (XII)). These needles are joined together by means of a horizontal rod suspended from O by a vertical torsion wire. The point O consequently remains fixed, so that the strip tends to rotate under the action of the surface pressure. It is brought back to its original position by means of the torsion head and the couple necessary to restore it is read off on a graduated circle. Adam <sup>3</sup> has replaced Langmuir's balance by a horizontal torsion wire.

In order that the strip may move without friction it is necessary to leave some play between its extremities and the edges of the frame. As a result there is a tendency on the part of the film to leak into the compartment B. To avoid this, Langmuir has used two air jets suitably directed towards the ends of the strip. More recently Adams and Jessop <sup>4</sup> have employed very thin and flexible platinum ribbons joining the extremities of the barrier to the edges of the frame. Instead of these platinum ribbons, Guastalla <sup>5</sup> has used fine silk threads coated with vaseline capable of floating on water (Fig. 40 (XII)). Their rigidity is negligible and they are very effective in setting a boundary to the spreading of a film. Using such methods, these workers have been able so to increase the sensitivity of their apparatus as to measure pressures down to a few thousandths of a dyne/cm.

The pressure/surface curves for films show points of inflexion or of discontinuity, the position and nature of which is difficult to determine by measurements made point by point. An apparatus which allows of continuous and automatic recording of the variations in surface pressure as a function of surface area, has been described by Dervichian <sup>6</sup> (Fig. 41 (XII)). He has adapted the old method of measuring surface tension due to Wilhelm. A microscope cover glass (*l*) joined at the edge to a glass rod is suspended vertically from one of the pans of a balance. The plate is partially immersed in the water contained in the trough. It is acted on by two opposite forces: (1) A pull towards the interior of the water which acts along the line of contact with the liquid. This force is due to the surface tension and is proportional to it. (2) The upward force due to the buoyancy of the water which will be proportional to the depth to which it is immersed. When equilibrium has been established for any position of the plate, a fall in surface tension (rise in surface pressure) will lead to the establishment of a new position of equilibrium for which the force due to buoyancy is less, the plate rising further out of the liquid. This displacement is transmitted to the balance. It is directly proportional to the increase in pressure and follows faithfully all its variations. Calibration is effected by placing weights of a few centigrams in the pan which carries

<sup>1</sup> *Proc. Roy. Soc.*, 1922, 101, 454.

<sup>2</sup> *Ann. de Phys.*, 10<sup>e</sup> sér., 4, 480.

<sup>3</sup> *Proc. Roy. Soc.*, 1926, 110, 435.

<sup>4</sup> *Ibid.*

<sup>5</sup> *Compt. rend.*, 1929, 189, 241.

<sup>6</sup> *Jour. de Phys.*, Sér. VII, 1935, 6, 221; *Ann. de Phys.*, 11<sup>e</sup> Sér, 1937, 8, 361.

the plate. A mirror ( $m$ ) supported on the axis of the beam of the balance reflects the light from a small lamp which is focused by a cylindrical lens ( $L$ ) or a strip of photographic paper wound round the recording cylinder  $C$ . This cylinder is rotated by means of a system of gears and is coupled to the moving barrier ( $p$ ) which compresses the film on the water surface. The whole is moved by a chain ( $Ch$ ) which is engaged by the driving shaft

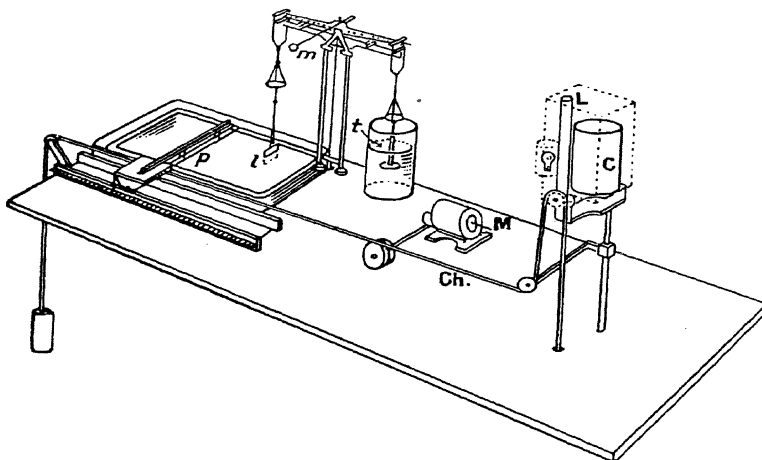


FIG. 41 (XII)

of an electric motor ( $M$ ). The photographic record when unwound shows the position of the barrier as abscissae and the displacements of the plate as ordinates, the latter being, of course, proportional to the variations in surface pressure. In order to diminish the sensitivity, the other pan of the balance supports a cylindrical rod ( $t$ ), which is partially immersed in vaseline oil. The upward force exerted will depend on the diameter of the rod but will always remain proportional to the vertical displacement of the plate.

**Isotherms of Monomolecular Films.** The general form of the isotherms obtained with films of different substances is shown in Fig. 42 (XII). At very great dilutions (several thousands of square Ångströms per molecule) the pressure, which is only of the order of a few hundredths of a dyne/cm., varies in proportion to the concentration. The curve representing this state of affairs approaches asymptotically the hyperbola  $PA = RT$  at low pressures ( $P$  = pressure,  $A$  = area per gram molecule,  $R$  = the gas constant,  $T$  = the absolute temperature). On continued compression, the horizontal portion  $BC$  appears, which is due to the transition from the two-dimensional vapour to a two-dimensional condensed phase. At  $B$  all the film has become liquid and the portion  $BA$  of the curve corresponds to the compression of a two-dimensional liquid phase. Collapse of the film occurs at  $A$ , and, on further compression, molecules leave the surface to form an ordinary three-dimensional state.

Solid layers exist for which the horizontal region of the isotherm corresponds to a passage from the gaseous to the solid state. Gaseous layers are also known which are above their critical temperature. Here no transitional region exists. Certain liquid layers may be solidified by compression.

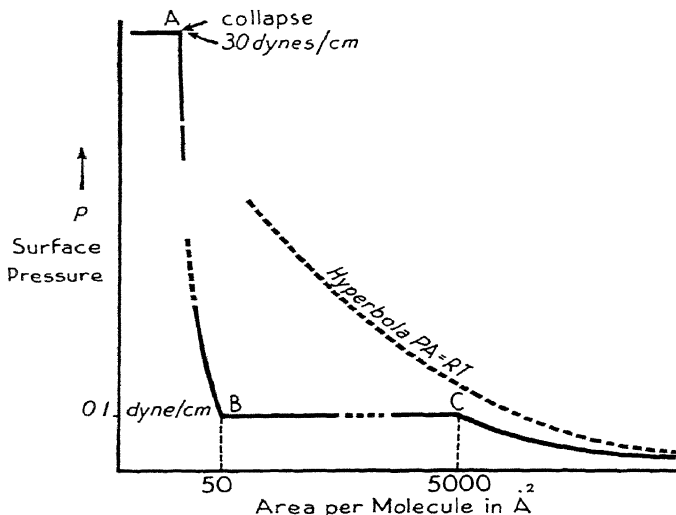


FIG. 42 (XII)

In such cases the curves after the horizontal portion due to liquefaction and at a higher pressure, show a second horizontal region corresponding to the passage from the liquid to the solid state. Finally, a fourth state may exist which is intermediate between the liquid and solid states and which is to be compared with the known liquid-crystalline state in three dimensions.

**Surface Potential of Monomolecular Films.** The electrical potential difference at the air-water interface undergoes a considerable fall (several tenths of a volt) when a monomolecular layer is spread on the water. This fall in potential which is a function of the concentration and the state of the film, has been studied in particular by Guyot,<sup>1</sup> Franklin,<sup>2</sup> Schulman and Rideal,<sup>3</sup> Adam and Harding,<sup>4</sup> Dervichian and O'Ceallaigh.<sup>5</sup> The method consists in ionizing the air between a metallic electrode and the surface of the water, and of measuring by a method of opposition, the potential difference between the poles of the 'gas cell' so formed, before and after spreading a film. In general, quadrant electrometers have been used, but Dervichian and O'Ceallaigh have employed an electrometer valve in conjunction with a galvanometer. By adapting this device to the apparatus for registering surface pressure differences, they were able to

<sup>1</sup> *Ann. de Phys.*, 10<sup>e</sup> Sér., 1924, 2, 506.

<sup>2</sup> *Zeit. d. Phys. Chem.*, 1925, 116, 486.

<sup>3</sup> *Proc. Roy. Soc., A*, 1931, 130, 259.

<sup>4</sup> *Ibid.*, A, 1932, 138, 411.

<sup>5</sup> *Jour. de Phys.*, 1935, VII, 4, 427 and 429.

record on the same photographic paper the variations in the potential difference as a function of the surface area (Fig. 43 (XII)).

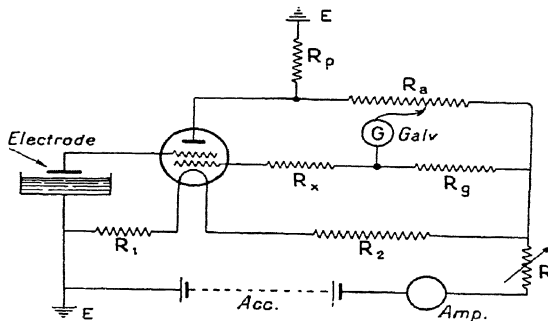


FIG. 43 (XII)

**The Building up of Polymolecular Layers from the Superposition of a Number of Monomolecular Films.** Langmuir and his co-workers<sup>1</sup> have introduced a new technique which opens out new horizons in the study of surface phenomena. Following the usual method, a film of stearic acid is spread out on the surface of water containing in solution a barium salt (0.01 grams per litre) and potassium bicarbonate (0.05 grams per litre). After a few minutes the fatty acid will have been transformed into a more or less acid barium stearate. It is necessary to maintain this layer under a constant pressure independent of the area it may occupy. To do this, the surface occupied by the film is bounded by a paper barrier capable of free movement along the edges of the dish. Behind this 'piston' barrier a film of oleic acid is deposited which is kept at the saturation point by a few drops of acid in excess. Under these conditions, as long as the layer of oleic acid remains saturated, it exerts a constant pressure on the 'piston' of 30 dynes per centimetre. This is transmitted to the stearic acid without any danger of the films mixing.

If a polished plate or disc of chromium plated metal be dipped into the stearic acid film and then withdrawn vertically, it will be found that a portion of the film leaves the water and attaches itself to the surface of the metal. Each time the disc is withdrawn the barrier which encloses the stearic acid surface will be seen to advance by an amount proportional to the surface of the disc. Each time the disc is dipped and then carefully withdrawn a new layer is deposited; one on dipping and one on withdrawal. After a few operations, the first interference colours will be seen to appear, and on continuing the action, one can run through the whole gamut of colours of the first order, and then those of the second order, &c. If different portions of the plate be dipped a different number of times, regions showing different interference colours may be obtained. Here we have in another form the stratified soap bubbles studied by J. Perrin with the incomparable

<sup>1</sup> Blodgett, *J. Amer. Chem. Soc.*, 1935, 57, 1007. Blodgett and Langmuir, *Phys. Rev.*, 1937, 51, 964.



advantage of being able to form at will layers of any desired thickness. In order to observe the colours it is necessary to examine the films at grazing incidence, preferably with a Nicol prism. These films may be seen on other metals or on glass provided that the index of refraction of the supporting substance is somewhat greater than that of stearic acid.

## SECTION 7: VISCOSITY<sup>1</sup>

When a fluid flows or when its form is altered, forces are called into play within the fluid which offer resistance to the force causing flow or change of form. This property of the fluid is known as *viscosity*, and fluids are referred to as mobile or viscous according to their tendency to flow readily or not. Viscosity refers only to forces within the fluid, being occasioned by the relative motion of contiguous portions of the fluid. It may thus be looked upon as *internal friction*. To consider the mechanism occasioning viscosity, take the case of a liquid flowing over a plane surface. The layer of liquid molecules in contact with the plane surface is attracted by the molecules of the material and there is definite evidence for the assumption *that this layer remains stationary*. The flow may then be considered as a sliding motion of contiguous layers over one another.

A layer at a distance  $d$  from the plane may be moving with a velocity  $v$ , parallel to the plane. The layer contiguous to this tends to be pulled forward by the attraction of the upper layer and at the same time retarded by the slower-moving layer beneath it, and so down to the surface layer which has zero velocity.

There is thus a force ( $f$ ), acting on a layer of the liquid, which is occasioned by the *relative velocities* of the layers above and below. The simplest assumption that can be made about this force is that it is proportional to the velocity gradient  $\frac{V_1 - V_2}{d}$  in the immediate neighbourhood of the plane. For unit surface area of liquid we then have  $F = \eta v$ , where  $\eta$  depends on the nature of the liquid and  $v$  is the velocity gradient. The constant  $\eta$  is known as the coefficient of viscosity and may be defined as the numerical value of the *tangential force per unit area per unit velocity gradient*. The unit of viscosity in the C.G.S. system is called the *poise*. The 0.01 part of this unit (i.e. the centipoise (cp.)) is used more in practice. The viscosity of water at 20° C is approximately 1 cp. (see page 81). The ratio of the viscosity (in poises) to density (in grams per cubic centimetre) is called the *kinematic viscosity*.

The need for accurate determination of the coefficient was for long overlooked. Of late years the importance of viscosity in determining questions of constitution, its relation to conductivity, and its importance in colloid chemistry, have made it a property well worthy of exact study. On the commercial side also, viscosity measurements are extremely necessary, as, for instance, in problems of lubrication. A large amount of research has, therefore, resulted in the perfection of a number of instruments for the determination of this coefficient. The flow of fluids in capillary tubes, the oscillations of a disc suspended in the fluid, the force required

<sup>1</sup> See page 120.

to displace surfaces close together in the fluid, have all been used as the basis of methods for this determination. In any method with this object the temperature control is essential, as viscosity decreases rapidly with rise of temperature.

The instruments used for the experimental determination of viscosity are known as 'glischrometers', the name given by Thorpe and Rodger in their memoirs, or, more commonly, viscometers. They may be divided into two classes, 'absolute' viscometers, by means of which the coefficient of viscosity is directly determined from the dimensions of the instrument together with a time interval, and 'secondary' or 'commercial' viscometers, where the result is obtained by comparison with a liquid of known viscosity (determined by means of an 'absolute' viscometer).

### ABSOLUTE VISCOMETERS

The absolute viscometers at present in general use depend upon the time of flow of the liquid through a capillary tube under a known pressure. The value of  $\eta$  is then obtained from the formula (proved on page 87)

$$V = \frac{r^4(p_1 - p_2)\pi}{8\eta l}$$

where  $V$  = volume of liquid passing a cross-section of the capillary in unit time

$r$  = radius of capillary

$p_1, p_2$  = pressures at beginning and end of capillary

$l$  = length of capillary

**Method of Thorpe and Rodger.** The first attempt to use this method with very great accuracy was that of Thorpe and Rodger. Their method, modified by different experimenters, is still a basic one. A diagram of their apparatus is given (Fig. 44 (XII)). The capillary, 0.008 cm. radius and 2 mm. wall thickness, was fused within the thin glass arms giving access to the liquid reservoirs. One of these was filled to the etched mark  $m_1$  or  $m_3$  and the liquid forced through the capillary by a manometrically measured external pressure until the meniscus reached the  $m_2$  or  $m_4$  mark. The meniscus was watched by means of a telescope with cross-hairs and the time of flow determined by a stop-watch. Great precaution was taken to ensure dust-free liquid, and the whole apparatus was brought to a constant temperature in a thermostat before a measurement.



FIG. 44 (XII)

The radius of the capillary was determined by weighing a pellet of mercury which occupied a measured length in the tube. This was performed after the fusion of the capillary to the rest of the apparatus, as was the determination of the length of the capillary. Under these conditions the processes are not easy to accomplish. In all viscosity measurements by the capillary-tube method, the simple formula must be modified to account for certain departures from the ideal conditions. A correction for the variation in the driving force due to the changing head of the liquid as it flows through the capillary must be introduced. Bingham, Schlesinger and Coleman<sup>1</sup> show that the true mean head to be added to the constant external pressure may be determined experimentally by measuring the times required for a given volume of liquid to flow (1) up and (2) down in the apparatus. The correction ( $x$ ) is then obtained from the formula

$$x = \frac{\eta}{2Cp} \left[ \frac{1}{t_1} - \frac{1}{t_2} \right] \cdot \frac{C_1}{2C} \left[ \frac{1}{t_1^2} - \frac{1}{t_2^2} \right]$$

where  $C$  and  $C_1$  are constants which may be calculated:

$$C = \frac{\pi r^4}{8lv}, \quad C_1 = \frac{1.12v}{8\pi l}$$

For ordinary work the mean of the hydrostatic head before and after the transpiration may be taken for this correction.

A correction must also be introduced for the pressure used in imparting kinetic energy to the liquid at the entrance to the tube; a further correction to the length of the capillary must be applied to compensate for the modification of the stream lines at the entrance to the tube. An addition of  $0.5d$  to the length ( $d$  = diameter) will approximate to this correction.

Thorpe and Rodger find it best to neglect this altogether. Their final corrected formula is

$$\eta = \frac{\pi r^4 t p}{8lv} - \frac{\rho v}{8\pi l t}$$

where  $p$  = applied pressure which may be corrected as above

$\rho$  = density of liquid

$v$  = volume flowing in time  $t$

The second term is the kinetic energy correction. Later research has introduced a factor  $m$  in this term. The value mostly accepted for  $m$  is that of Boussinesq, who gave the coefficient 1.12 for a capillary with a rounded entrance.

The apparatus of Thorpe and Rodger has been criticized on the grounds that it is difficult to construct and to clean, and that the radius of the capillary is difficult to determine after its fusion to the reservoirs. They use the capillary ground (not fused) into the reservoir arms (Fig. 45 (XII)). These workers recommend a capillary 0.025 cm. diameter and 10 cm. long and a volume of 2.6 ml. for the bulbs. With this form of apparatus the coefficient of viscosity can be found to an accuracy of about 0.1 per cent.

**Stone's Viscometer.** A very convenient form of absolute viscometer is described by Stone.<sup>2</sup> The pressure is supplied by a column of mercury

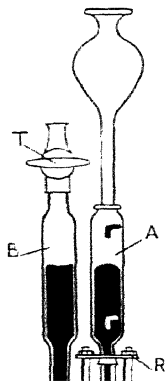
<sup>1</sup> *J. Amer. Chem. Soc.*, 1916, 38, 27.

<sup>2</sup> *Engineering*, November 26, 1915.



FIG. 45 (XII)

automatically maintained at a constant head. The instrument consists of three essential elements, viz. the viscometer burette, the adjustable constant head apparatus, and the pressure gauge. The viscometer burette (Fig. 46 (XII)) consists of two glass vessels A and B of equal internal diameters and suitable length connected at their lower ends by means of a wide-bore tube C, and also a capillary D of suitable dimensions for the desired purpose. The selected capillary has ground-tapered ends which fit into the ground ends of the other portions of the burette, all ground joints being made to a special size and taper so as to be interchangeable. The three portions of the burette are held together by the brass clips and tension rods R.



C

R

FIG. 46 (XII)

The measuring burette is fitted with two platinum wires sealed into its wall and so bent that a portion of each wire lies approximately on the axis of the tube. The capacity of the burette between the platinum points is determined from the weight of mercury required to fill the space between them. A glass tap is provided at the air inlet to the burette to control the starting of the test. The whole of the burette is immersed in water contained in a glass tube with a brass bottom, the joint from brass to glass being held by a rubber ring. A brass cap with the requisite slot for the insertion of the burette and holes for a thermometer, stirrer and an extension to the measuring burette is provided. The water in the container is heated by a Bunsen burner.

**Constant-head Apparatus** (Fig. 47 (XII)). The adjustable constant-head apparatus consists of two glass vessels, the lower one being furnished with a tap at the top and the upper one suspended by a spring from a hook attached to a sliding clip which can be clamped to the glass at any desired height. Through the outer end of the clip a glass siphon pipe passes to the bottom of the upper vessel, when the latter is at its highest point, i.e. against the clip. The siphon is connected to the lower vessel by means of a rubber tube. The strength of the rubber spring is so adjusted that as the mercury flows from the upper to the lower vessel, the former, being thereby

lightened, will rise so as to maintain the surface of the mercury in it at constant height above that of the mercury in the lower vessel.

The pressure gauge is of the ordinary U pattern, with mercury as the working fluid and a millimetre scale between the limbs. A three-branch pipe connects the burette, pressure gauge and constant-head apparatus.

#### Method of Working.

The instrument must be set up vertically. The fluid to be tested is fed into the burette by means of a pipette, which is marked to indicate the correct quantity of fluid. As the liquid flows into the lower vessel the burette is removed from the socket and raised sufficiently to reduce the air pressure and draw in the fluid well below the point of the lower gauge wire. The tap is then closed and the pressure apparatus adjusted to give the required pressure. The tap is next opened and the time between the contacts of the fluid meniscus with the ends of the gauge wire taken by means of a stop-watch or other suitable chronograph. The burette is easily cleansed by removing it from the water-bath and rinsing with a mixture of alcohol and ether.

If the quantity of fluid put into the burette is such that when it is at the same level in both legs it is also half-way between the platinum points; for approximate measurements no correction need be made for the fluid head in the burette or for the density of the fluid, provided the constant pressure be not reduced below 3 cm. of mercury.

For a high degree of accuracy the initial fluid head in the burette is adjusted to compensate for the variation in the total head caused by the changing levels of the fluid in the limbs of the burette.

The value of  $\eta$  may then be calculated from the usual formula, the pressure used, the volume of the burette and the time of flow being known. The dimensions of the capillary tube may be determined as usual by weigh-

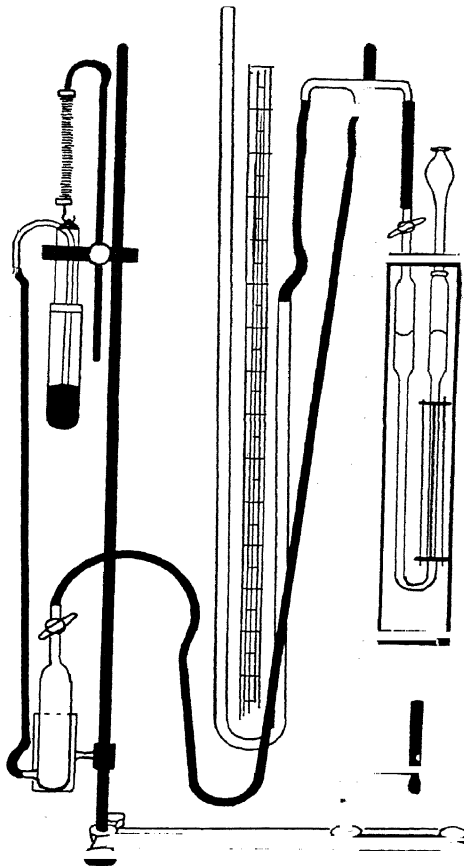


FIG. 47 (XII)

ing its mercury content. For accurate work the correction for the 'end' errors must be taken into account as previously described.

For the determination of viscosity in absolute units the British Engineering Standards Association have published particulars of simple, rapid and accurate methods for the determination of the viscosity of a liquid in C.G.S. units. Specifications have also been drawn up for a suitable standard apparatus for normal liquids, but not for heavy thick lubricants or colloidal solutions in which factors other than viscosity are involved, e.g. rate of shear, thermal history or mechanical treatment.

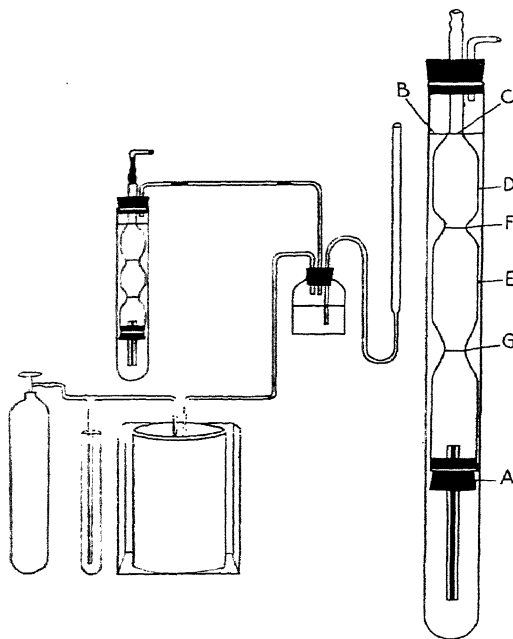


FIG. 48 (XII)

#### High Viscosity Measurements.

In determining the viscosities of very viscous oils, e.g. castor oil, it is advisable to use wide capillary tubes. An apparatus in which capillary tubes up to 1.5 mm. diameter are used is described by Barr<sup>1</sup> (Fig. 48 (XII)). A low pressure is used which is conveniently measured by means of a water manometer. This increases the hydrostatic pressure correction. The method of correction used by Bingham, Schlesinger, Coleman (*loc. cit.*) can be applied. It is probable that the use of wide capillaries minimizes the error in the evaluation of the radius of the capillary.

#### High-pressure Measurements.

The effect of very high pressures on the viscosity coefficient has been investigated carefully by Hyde<sup>2</sup> at

the National Physical Laboratory. Slight changes in the viscosity of liquids under pressures of a few atmospheres had previously been noted. Hyde, using pressures up to 1,100 atm., found the viscosities of mineral oils to increase to more than ten times their value at one atmosphere. A sketch of his apparatus is appended (Fig. 49 (XII)).

**The Instrument.** It consists of a U-tube, the limbs A and B being connected together at their lower ends by a large-bore tube and at their upper ends by a capillary tube. The whole is mounted on a frame supported by a knife-edge D, and so arranged that the left-hand side is heavier than the right. The lower half is filled with mercury and the upper half with the liquid under experiment. The motion of the frame is governed

<sup>1</sup> Aero. Research Committee Reports, 1924, No. 906.

<sup>2</sup> *Proc. Roy. Soc.*, 1920, A, 97, 240.

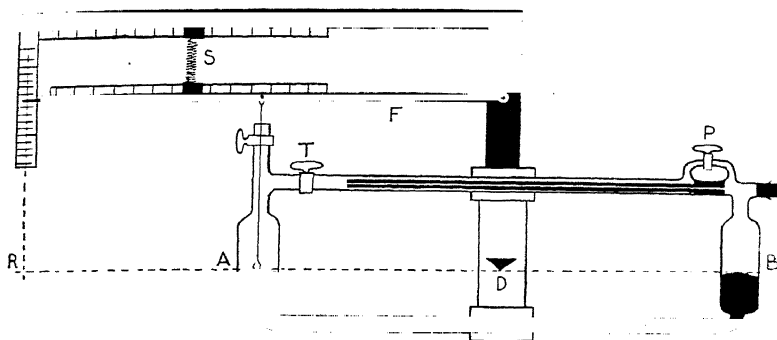


FIG. 49 (XII)

by the extension of a spring *S*, to which it is connected through the arm *F* which terminates in a pointer moving over a fine scale. In making an experiment the tilting frame is set in such a position that the horizontal tubes are level and the scale adjusted so that the pointer is at zero. A tilt is given to the frame by moving the pointer vertically upwards, the taps *T* and *P* being open. The tilt causes a flow in the U-tube, and when this flow has ceased the taps are closed and the frame restored to its original position with the pointer at zero, the tension of the spring being adjusted to support the frame in this position. The head of mercury in the circuit tending to cause flow around it can be calculated from the motion which has been given to the pointer end from the distances *DR* and *AB*. If now the tap *T* be opened the liquid will flow through the capillary tube from *A* to *B* and the mercury from *B* to *A*. The spring is so designed that the displacement of the frame due to the flow of mercury from one vertical limb to the other is such that the head of mercury producing the flow is constant and the fall of the frame, as indicated by the movement of the pointer over the scale, gives a measure of the volume of the liquid which passes from one side to the other. In this way the whole of the data required for the calculation of the coefficient of viscosity is available when the dimensions of the capillary are known and  $\eta$  is obtained from the simple formula

$$\eta = \frac{\pi \rho h r^4 t}{8 v l}$$

*h* being the head of liquid and the other symbols having their usual meaning.

The formula requires a knowledge of the density of the liquid under the working pressure and a method for the determination of the latter is described in the original work. Special steel was used in the construction of the parts subjected to pressure.



## RELATIVE VISCOSITY

**Ostwald's Viscometer.** The labour involved in determining the constants of the apparatus in the absolute viscometer, has led to the method of calibrating the viscometer by means of a standard liquid. The outstanding relative viscometer in general use is that of Ostwald (Fig. 50 (XII)). It consists of a U-tube, part of one arm being a capillary tube. Above the capillary in the same arm is a bulb. The other arm is a wide tube in which also is a bulb. Two marks are etched on the glass, one above and one below the bulb over the capillary. A given volume of liquid is placed in the instrument and the time measured that is required for the meniscus of the liquid to pass the two marks under the force of gravity only. If  $\eta_0$  is the viscosity of the standard liquid and  $\eta_i$  of the given one, then from the ordinary formula

$$\eta = C_2 p t - \frac{C_1 \rho}{t}$$

$C$  and  $C_1$  being constants for the instrument,

$$\eta_0 = C_2 p_0 t_0 - \frac{C_1 \rho_0}{t_0}$$



FIG. 50 (XII)

then if  $\eta_i$  is nearly equal to  $\eta_0$ , or if  $t$  and  $t_0$  are very large, it is approximately true that  $\frac{\eta_i}{\eta_0} = \frac{pt}{p_0 t_0}$ , and since the pressure is proportional to the densities we have  $\frac{\eta_i}{\eta_0} = \frac{\rho t}{\rho_0 t_0}$ , which formula is suggested by Ostwald.

The formula is true for dilute solutions when water is taken as the standard.

There are a number of disadvantages in the Ostwald instrument. The driving pressure is variable, and the times for different liquids may vary over a very wide range. The water constant of the apparatus also varies; four reasons have been assigned for this:

- (1) Solid particles blocking the capillary
- (2) The solvent action of water and cleaning liquids on the walls of the capillary
- (3) The temperature hysteresis
- (4) The contamination of the water by dissolved glass

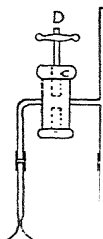
**Quartz Viscometer.** For the above reasons an improved Ostwald viscometer made entirely of fused quartz has been constructed by Washburn and Williams. This instrument eliminates the errors given above and with it relative viscosities are obtained to 0.01 per cent with proper timing and temperature-control arrangements. The following is a short description of the instrument (Fig. 51 (XII)).

The capillary was of diameter 0.05 cm. and length 19.5 cm. The volume of the bulb A was 9 ml., and the bulb B was 4.5 cm. high and 8.0 cm. wide. The mean head of the liquid used was 20 cm. The liquid is introduced by a 65 ml. pipette and the three-way cock attached as shown, and the instrument immersed in the thermostat. The cock is turned to connect D with

VISCOSITIES OF SOME COMMON LIQUIDS IN C.G.S. UNITS

Liquid	Temperature, ° C.	Viscosity
Alcohol ethyl	0	0.01843
	10	0.01525
	25	0.01084
	50	0.00715
Alcohol methyl	0	0.00834
	10	0.00715
	20	0.00611
	35.7	0.00483
Benzene	0	0.00906
	10	0.00746
	20	0.00642
	60	0.00389
Chloroform	0	0.00706
	20	0.00568
	30	0.00513
	40	0.00467
Carbon tetrachloride . . . .	0	0.01351
	14.9	0.01053
	35.2	0.00793
Ether	2.4	0.00287
	11.2	0.00279
	15	0.00256
	20	0.00226
Ethyl acetate	0	0.00581
	10	0.00504
	20	0.00451
	46.2	0.00338
Ethyl formate.	0	0.00508
	20	0.00403
	25	0.00379
Glycerine	25	13.10
Glycol .	25	0.1733
Pyridine	25	0.00878
Water .	0	0.01775
	10	0.01309
	20	0.01012
	50	0.00550
	60	0.00474
	90	0.00321
	100	0.00297

the capillary arm of the viscometer and suction applied till the bulb A is filled. The cock is then closed and turned to connect E with F. The time of the flow is taken by an automatic apparatus controlled by a standard clock. Such an exceedingly delicate apparatus is only necessary for very refined working.



**Bingham's Viscometer.** Bingham<sup>1</sup> describes an instrument (Fig. 52 (XII)) having the obvious advantages of the Ostwald instrument and overcoming many of its objections. The volume K is made as nearly as possible equal in volume, similar in shape, and at the same height as C. The working volume is contained between A and H, and the volume of flow between B and D. External pressure is supplied by compressed air and measured with a manometer. The time measurement is made as the meniscus passes either from B to D or from D to B, depending on the direction of flow. The corrections are made as for absolute measurements and the viscosity calculated from the formula

$$\eta = Cpt - C' \frac{\rho}{t} \quad \} \quad \}$$

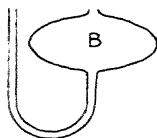


FIG. 51 (XII)

In obtaining the pressure correction, due to the average resultant hydrostatic pressure in the viscometer,  $C'$  can be estimated accurately enough by simple measurements. The value of  $C$  can be estimated by assuming  $p_0 = p$ . The value of the hydrostatic head ( $x$ ) being known, the true value of  $C$  may be calculated from an observation upon the time of flow of any liquid whose viscosity is accurately known. For freshly distilled water at 20°

$$C = \frac{0.01005t + C'\rho}{pt^2}$$

By direct measure

$$C = \frac{384.8r^4}{V \cdot l}$$

If  $g$  does not equal 980 the value of  $C$  must be increased 0.1 per cent for each unit in excess.

The value of  $C'$  is determined from

$$C' = \frac{0.0446V}{l}$$

In these calculations

$V$  = volume of bulb C between the marks B and D

$l$  = length of capillary

FIG. 52 (XII)

<sup>1</sup> See *Fluidity and Plastic Flow*, 1922.

For the commercial determination of the relative viscosities of lubricating and other oils a viscometer of the Redwood type may be employed. In its simplest form it consists of a glass pipette with a mark on the tube to which oil is filled. On allowing the oil to flow out, the time of flow is noted, and compared with that for standard oil. In this way a comparative viscosity figure for the oil is obtained. The Saybolt instrument is of a somewhat similar type. In viscometers of the Redwood type the head causing the flow is the hydrostatic head of the liquid and is fixed by the construction. In such viscometers a formula of the type  $v = A \times T - \frac{B}{T}$

holds within certain limits,<sup>1</sup> when  $v$  is the kinematic viscosity of a liquid for the flow of a fixed volume of which a time  $T$  is required and  $A$  and  $B$  are constants for a given instrument. The National Physical Laboratory method of determining corrections for the Redwood viscometer has been described and illustrated by a chart.<sup>2</sup> Conversion formulae for the Redwood, Saybolt and Engler viscometers are given in the British Engineering Standards Association publication No. 188—*Determination of Viscosity in Absolute Units*.

**Falling-sphere Viscometer.** For the comparison of the viscosities of a large number of liquids, the falling-sphere method is very rapid. The method is much used in industrial practice. The time of fall of a sphere in the liquid has long been recognized as an approximate measure of viscosity, but the work published by Gibson and Jacobs<sup>3</sup> places it in the ranks of exact methods. The velocity of a sphere falling vertically in a fluid in relation to viscosity was investigated mathematically by Stokes, who derived the well-known equation

$$V = \frac{2}{9} g r^2 \frac{\rho - \sigma}{\eta}$$

where  $V$  = velocity of sphere,  $r$  = radius,  $\rho$  = density of sphere,  $\sigma$  = density of liquid,  $g$  = the gravity constant (980) and  $\eta$  = viscosity of fluid. For practical working two corrections must be introduced: (1) a correction for the confined space of the liquid, i.e. the nearness of the wall of the vessel influences the velocity; and (2) the 'end effect' of the bottom of the tube on the velocity. The complete equation for the fall is then

$$9\eta S(1 + 2.4x)(1 + 3.3r/h) = 2gr^2(\rho - \sigma)T$$

where  $T$  is the time taken for the sphere to fall through a distance,  $S$ ,  $x$  = the ratio of the radius of the sphere to that of the cylinder, and  $h$  is the height of the liquid.

This equation can be used to give an absolute measure of viscosity.

For comparative measurements the times of fall with identical instruments for different liquids can be measured. Then the equation

$$\frac{\eta}{\eta_1} = \frac{\rho - \sigma}{\rho - \sigma_1} \cdot \frac{T}{T_1}$$

gives the comparative viscosities when the densities are known. A liquid of known viscosity can then be used as a standard.

<sup>1</sup> Barr, *J. Sci. Inst.*, 1930, 1, 359–61.    <sup>2</sup> *Ibid.*    <sup>3</sup> *J. Chem. Soc.*, 1920, 117, 473.

A diagram of the apparatus is given (Fig. 53 (XII)).<sup>1</sup> In the choice of a sphere uniformity of diameter is most important and steel ball-bearings have been found satisfactory. These are guaranteed to be correct within 0.0025 mm. A ball of 0.15 cm. in diameter was chosen as the standard size. The density of the steel was found for one gross of balls. The total length of the tube is 29 cm., divided into three 5 cm. lengths for measurement of the time of fall, and another 5 cm. to allow it to acquire its uniform velocity. A further graduation mark fixes the level of the liquid. To

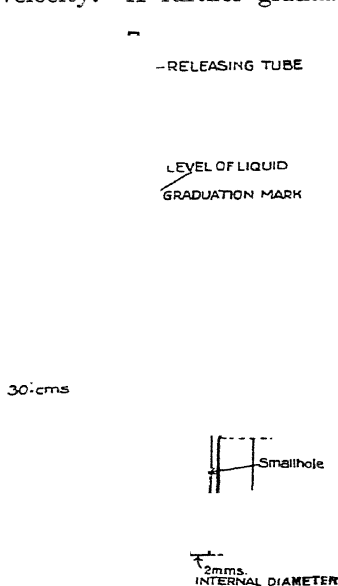


FIG. 53 (XII)

deliver the sphere into the centre of the tube, the latter is closed with a stopper bored centrally with a glass tube of 3 mm. internal diameter and 7 cm. long passing through. This tube is adjusted to dip 3 cm. below the surface of the liquid in the viscometer tube. The sphere when dropped into the releasing tube travels very slowly down it and is freed from air-bubbles; it then leaves the end below the surface of the liquid with the minimum of disturbance and in the centre of the tube.

With dark or coloured solutions in which the fall of the steel ball cannot be seen there is a simple device to overcome the difficulty.<sup>2</sup> A simple oscillating radio circuit is employed. Two pairs of inductance coils are wound in two slots on the viscosity tube, and so separated that their centres are divided by the distance through which the flight of the ball is to be measured. The circuit is set oscillating and adjusted to give the desired frequency. When the ball goes through the coils a change of note is observed.

A number of technical instruments are in use in different countries. The better known are the Engler Viscometer in Germany, the Redwood Viscometer in Great Britain, and the Saybolt Viscometer in the United States. Most of them are devised with the idea that the time of flow through an opening of a given quantity of liquid is proportional to the viscosity. Of late, correction tables for each instrument have been drawn up to convert the readings into true viscosities. Even so these instruments are not generally suitable for precise work in physical chemistry.

**Viscosity of Colloidal Solutions.** With colloidal solutions the use of a glass capillary is often inadvisable. The method of the falling-sphere is only applicable when a large amount of solution is available. Moreover,

<sup>1</sup> Research Dept., Woolwich Rept., Report No. 22, Part III. (The releasing tube (Fig. 53 (XII)) is an improvement on that described in the original paper.)

<sup>2</sup> Symmes and Lantz, *J. Ind. and Eng. Chem.*, 1930, 5, 35.

the capillary method does not permit of continuous observation of the variations or of the influence of temperature or time. In the P. Lecomte du Noüy<sup>1</sup> viscometer these difficulties are overcome. The instrument is based on the principle of two coaxial cylinders, the outer cylinder or cup, which contains about 1 ml. of the solution to be studied, is rotated at constant speed and the inner cylinder, or bob, is suspended by means of a galvanometer wire. A mirror supported by the suspension, a lamp and a scale for the readings and a thermostatic arrangement are the only other apparatus required. The viscometer has been extensively employed for the examination of colloidal solutions, e.g. normal blood serum.

Noüy describes the carrying out of a series of experiments as follows: 'The serum was poured into the cup (1 ml.) and the bob lowered into the serum. The zero being checked, the motor was started, and a first reading made at the starting temperature (between 20° and 25°). After checking the zero again, and repeating this measurement at least 3 times, with an interval of 5 minutes between each reading, the heating current was put on. (A current of 1 ampere through a resistance immersed in the oil surrounding the cup brought the temperature up from 20° to 70° in about 45 minutes.) Then the readings were taken, and recorded simultaneously with the temperature. A telescope placed alongside the scale makes this possible. As a rule, unless some critical point was neared or some unforeseen phenomenon occurred, readings were taken every 2°. The current was left on until the temperature of 70° was reached, in the first series of experiments; in other experiments the heat was stopped after a certain temperature had been reached (50°, 55°, 56° to 60°) and the oil allowed to cool by itself. As a rule, in order that the cooling from, say, 55° to 20°, should take about the same time as the heating from 20° to 55°, cold water was made to circulate in the double wall of the oil bath, and the rate controlled accordingly.' The results were plotted.

The ordinates express the readings on the scale, and therefore are arbitrary figures, but proportional to the absolute viscosities, the corresponding reading being the temperature.

**MacMichael Viscometer.** This instrument as shown in Fig. 54 (XII) consists of a steel ball ( $\frac{3}{4}$  inch to 1 inch diameter) fitting into a steel cup. The latter is fixed to a hollow stem to carry a thermometer. On the inner surface of the cup are three small projections (0.0001 inch) which keep the ball at a definite distance from the surface. A few drops of oil are placed in the cup and the ball placed in position and pressed down—air being excluded. The apparatus is then lifted vertically and the times from lifting until the ball drops off are noted by a stop watch. This period is related to the viscosity of the oil, and if the periods for two oils are taken a ratio of the viscosities of the two oils can be made. The functioning of the instruments depends on the slow creeping of the oil between the ball and cup. If the above apparatus is immersed in oil, surface tension effects at the edge of the oil film are avoided, and more accurate results obtained.



FIG. 54 (XII)

<sup>1</sup> *J. Gen. Physiol.*, 1923, 5, 429; 1929, 12, 3, 363.

The apparatus is claimed to be accurate to within 4% and is useful for rapid commercial work.

A large number of viscometers and plastometers have been described suitable for use with very viscous materials such as starch paste or gelatine.<sup>1</sup>

In the MacMichael viscometer a plunger of standard size is used. It is suspended by a torsion wire above the instrument. The glue is placed in a cup which is rotated at a constant rate of speed on a motor-driven platform. The viscosity determines the amount of twist on the wire, and this is measured on a graduated disc which is attached to the spindle. In the Stormer viscometer the speed attained by a cylinder which rotates in a cup by means of a falling weight acting through a spindle, gear and pinion is measured. A revolution counter is attached to the spindle which supports the cylinder. The results are not affected by the presence of solid particles.

In the Buel apparatus the rate of flow through a glass funnel with a lip is measured. This is generally employed with slightly alkaline pastes. In the Saare instrument the relative viscosity is calculated from the force required to withdraw a disc from a starch paste in which it is embedded.

**The Stormer Viscometer (Cenco)** determines viscosities by measurement with a stop-watch of the time required for a definite number of revolutions of a hollow rotating cylinder immersed in a test-cup provided with two vertical side vanes, a vertical central baffle and a thermometer holder. The test-cup is maintained at the desired temperature by means of a water or oil bath.

The rotating cylinder is driven by gearing operated by a falling weight: this consists of a box weighing 28 grams and when filled with lead shot 153 grams. A weight of 100 grams is convenient for measuring viscosities in the neighbourhood of 50 cp.

Relative viscosities are obtained by dividing the time required for the cylinder to make a specified number of revolutions—there is a revolution counter on the spindle of the cylinder—in the material under examination, by the time required for the cylinder to make the same number of revolutions in water at the same temperature and with the same operating weight. A calibration table giving the results in centipoises can be worked out.

## THE SIZE, VELOCITY, MEAN FREE PATH, AND COLLISION FREQUENCY OF MOLECULES

**The Avogadro Number.** Some very interesting calculations may be made from the viscosity of a gas determined at two different temperatures. Sutherland has established the following formulae:

$$L = \frac{1}{\sqrt{2} \cdot n\pi\sigma^2(1 + B/T)} \quad (1)$$

$$\eta = \frac{0.3503\rho\Omega}{\sqrt{2} \cdot n\pi\sigma^2(1 + B/T)} \quad (2)$$

<sup>1</sup> *Chem. Zentr.*, 1924, 2, 557.

where  $L$  = the mean free path of the molecules in centimetres  
 $n$  = the number of molecules in 1 ml. of gas at  $0^\circ$  and 760 mm.  
 pressure: this number multiplied by the number of milli-  
 litres in a gram molecule gives the Avogadro constant  $N$   
 $\sigma$  = the diameter of the molecule in centimetres  
 $B$  = the Sutherland constant  
 $T$  = the absolute temperature  
 $\eta$  = the viscosity in poises  
 $\rho$  = the density of the gas in grams per millilitre  
 $\Omega$  = the mean molecular velocity in centimetres per second

$$\begin{aligned}\text{also} \quad \Omega &= 0.921 \, G \\ &= 0.921 \sqrt{3RT}\end{aligned}$$

where  $G$  = the square root of the mean square of the molecular velocity  
 $R$  = the gas constant  
 hence equation (2) may be written

$$\eta = \frac{A\sqrt{T}}{1 + B/T}$$

where  $A$  is a constant.

If  $\eta_1$  and  $\eta_2$  are the viscosities of the gas at the two temperatures  $T_1$  and  $T_2$ ,

$$\frac{\eta_1}{\eta_2} = \frac{1 + B/T_1}{1 + B/T_2} = \frac{T_1^{3/2}}{T_2^{3/2}} \cdot \frac{(T_2 + B)}{(T_1 + B)} \quad (3)$$

A value for the Sutherland constant  $B$  can thus be found from equation (3), and then equation (2) can be used to obtain a value for  $n\sigma^2$ .

This last may now be used in equation (1) to calculate a value for  $L$ , *the Mean Free Path of the Molecules*, or this can be obtained from the equation  $L = 1.789\eta/\sqrt{\rho p}$ ,  $p$  being the pressure of the gas in dynes per square centimetre.

Knowing  $n\sigma^2$ , we can calculate a value for  $\sigma$ , *the Diameter of the Molecule*, if we assume that  $n$  has the value  $2.75 \times 10^{19}$ : but we can get approximate values of both  $n$  and  $\sigma$  in the following ways.

First making use of the so-called *Limiting Density* of the gas, that is to say the density of the densest known form; call this  $D$ .  $\pi\sigma^3/6$  is the volume of a spherical molecule and  $D$  being the density of that form in which the spaces between the molecules are a minimum,  $\pi\sigma^3 \cdot D/6$  will not differ greatly from the mass of one molecule. Also if  $\rho$  is the mass of 1 ml. of gas at N.T.P., and  $n$  is the number of molecules therein,  $\rho/n$  is the mass of one molecule.

$$\begin{aligned}\text{Hence} \quad \pi\sigma^3 \cdot D/6 &= \rho/n \\ n\sigma^3 &= 6\rho/\pi D\end{aligned}$$

Knowing  $n\sigma^2$  and  $n\sigma^3$ , we can get both  $n$  and  $\sigma$ ; multiplying  $n$  by 22400 we get the *Avogadro Constant*  $N$ .

$n\sigma^3$  can also be obtained from the value of  $b$ , the constant in Van der



Waal's equation, since  $b$  is four times the actual volume of the molecules ; i.e.

$$b = 2\pi n\sigma^3$$

Finally, from  $\Omega$  and  $L$ , the mean molecular velocity and the mean free path, we can calculate the *Collision Frequency*, that is, the average number of collisions per second for each molecule,

$$\gamma = \Omega/L$$

### VISCOSITY OF GASES

**Viscosity of Gases—Anderson's Method.** A simple means of measuring the viscosity of gases has been devised by Anderson, using an apparatus very similar to that employed in the ordinary air thermometer. A bulb furnished with a vertical tube communicates with a long capillary tube of uniform bore which can be opened or closed by means of a pinch-cock. (If the connexion from bulb A to tube B were vertical instead of horizontal in Fig. 1 (X), it would be suitable for the experiment. The capillary is fitted at D.) The volume of the bulb to B is known. Let the pinch-cock be closed and suppose the levels of the mercury to be at B and C. The difference is read off on the scale. The pinch-cock is then opened so as to let the air or other gas escape, and the outer tube lowered so that the level of the mercury in the other tube always remains at B. After the lapse of a measured time the pinch-cock is closed and the difference in level of the surfaces of the mercury again read off. These observations are sufficient to determine the coefficient of viscosity provided the length and cross-section of the capillary are known. Let  $V$  = the volume of the bulb to the mark B. Strictly  $V$  should be the volume of the bulb together with that of the capillary tube. This volume is kept constant during the experiment. Then if  $p$  is the pressure of the gas in the bulb at any instant

$$-V \frac{dp}{dt} = \frac{(p - P)\pi r^4}{16\eta l}$$

where  $P$  is the atmospheric pressure,  $r$  the radius of the capillary tube,  $l$  the length and  $\eta$  the coefficient of viscosity. Hence—

$$\log \frac{p}{p - P} = \frac{\pi r^4 P}{8\eta l V} t + \text{const.}$$

$$\text{or} \quad \log \frac{p + P}{p - P} = \frac{P}{\eta} k t + \text{const.}$$

where  $k = \left( \frac{\pi r^4}{8lV} \right)$  may be regarded as the constant of the apparatus.

Thus if  $p_1$  is the pressure at the beginning of the experiment,  $p_2$  the pressure at the end, and  $t$  the time,

$$\log_e \frac{(p_2 + P)(p_1 - P)}{(p_1 + P)(p_2 - P)} = \frac{P}{\eta} t \cdot k$$

from which  $\eta$  may be easily calculated.

In the determination of the coefficient of viscosity of a gas the fundamental idea is the same as for liquids. The method used by Lord Rayleigh in his investigations on argon and helium depended on the passage of the gas through a capillary tube under pressure. Two gas pipettes and manometers were connected by a capillary tube of very small bore and about 1 metre long. The volume of gas used was about 100 ml. and was caused to pass by a pressure of a few centimetres.

Then the formula is

$$V = \pi t \frac{p_1^2 - p_2^2}{2p_2} \cdot \frac{r^4}{8\pi l}$$

where  $(p_1 - p_2)$  is the pressure,  $t$  the time of transpiration, and  $r$  the radius of the capillary. A detailed description of this method is not appended, as its use has been superseded by the method devised by A. O. Rankine.

**Rankine's Apparatus.** Rankine's method is also a capillary tube one, the driving force being supplied by a pellet of mercury falling under gravity. A diagram of the apparatus is given (Fig. 55 (XII)). The capillary tube is about 50 cm. long and 0.2 mm. internal diameter. The other limb in which the mercury pellet falls is also about 50 cm. long, and of diameter as large as is compatible with keeping the mercury pellet intact. A diameter of about 3.5 mm. is suitable. The total length of the instrument is about 70 cm. and breadth 5 or 6 cm. Two taps Y and Z at the ends allow easy cleaning of the apparatus. Two marks  $y$  and  $z$  are etched on the wide tube so that they are symmetrical from the view of volume. This is done by admitting a certain volume of mercury and allowing it to occupy each end of the instrument in succession. The marks are then placed at the respective surfaces. The whole is mounted symmetrically on a board which is pivoted at its centre so that the tubes may be put at any desired angle. A thermometer is also attached to the board. The capillary tube is calibrated before inclusion in the apparatus and the mean value of the fourth power of the radius obtained. The volume between the marks  $y$  and  $z$  is obtained by weighing the quantity of mercury occupying this volume.

In making a measurement the apparatus is evacuated and the gas under experiment admitted. About 5 grams of mercury is then admitted. The time taken for the rear end of the pellet to fall between the marks  $y$  and  $z$  is noted. The instrument is inverted and the time taken for the fall in the opposite direction.

An average of a number of such times is used for the calculation. The times may be measured by a stop-watch corrected by a standard clock. Some of the mercury may be run off and weighed and the measurements repeated with the remaining pellet. Finally, the remaining mercury is run off and weighed. The apparatus should be placed in a constant-temperature bath during the measurements.

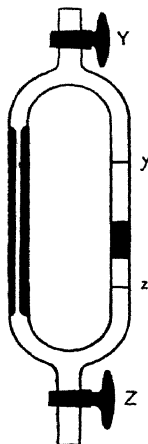


FIG. 55 (XII)

The value of the coefficient is calculated from

$$\eta = \frac{\pi p r^4 t}{8 l v}$$

$r$  = radius of capillary tube

$p$  = difference in pressure on two sides of mercury

$l$  = length of capillary

$v$  = volume swept out by mercury

$t$  = time of fall

Owing to capillarity  $p$  is not proportional to the length of the pellet. If observations are taken with different lengths of mercury it is found that a relation between the mass of the pellet and the time of fall can be represented by an equation

$$m = a + \frac{b}{t}$$

$a$  and  $b$  being constants.

If  $A$  = cross-section of tube (for a particular gas)

$\frac{mg}{A}$  = pressure, but  $\frac{gb}{At}$  only is used in forcing the gas through the capillary.

Hence  $p$  in equation =  $\frac{gb}{At}$

The final equation then is

$$\eta = \frac{\pi r^4 g b}{8 l v A}$$

The effusion apparatus described in the chapter on the density of gas may be used to determine the viscosity of gases. The gas is not passed through the opening N but through a long capillary U-tube which is connected by a two-way tap at F and connected with the top horizontal tube with a second tap.

## SECTION 8 : PRESSURE

The measurement of pressure may well be included in the list of fundamental physico-chemical processes. The number of investigations in physics or chemistry independent of a pressure measurement is only a small percentage of the whole. Gravitation and material kinetic energy bring a pressure factor into almost every problem. Most of the physical and chemical properties of matter, boiling-points, melting-points, physical state, chemical reactivity, &c., are dependent on the pressure and cannot be stated without reference to a measurement of pressure. Exact methods of measuring pressure, consequently, are essential to physico-chemical investigation.

**Units of Pressure.** Pressure is defined as a force per unit area. On the C.G.S. system the unit of pressure is the *dyne per square centimetre*. The British unit used in engineering practice generally is the *pound weight per square inch*, usually incorrectly written *pound per square inch*. More common in scientific work than either of the above units is the unit in terms of the height of a column of standard liquid. This unit is used owing to the general use of liquid manometers in pressure measurements. The standard liquid is mercury. The pressure is then expressed as so many inches, centimetres or millimetres of mercury; this means that the pressure per unit area is the weight of a column of liquid so many inches, centimetres or millimetres in height and of unit area cross-section. This is of course dependent on the temperature of the liquid and on the gravitational constant  $g$ . In low-pressure measurements the *millimetre of mercury* is the standard unit. For high-pressure measurements a larger unit is convenient. The one used is the 'atmosphere', or normal atmospheric pressure, i.e. the pressure due to a column of mercury 760 mm. high at  $0^\circ$ . A pressure of 100 atm., therefore, means a force per square centimetre of  $76 \times 100 \times d \times 1 \times g$  dynes, where  $d$  = density of mercury at  $0^\circ$ ,  $g$  = acceleration due to gravity.

Another absolute-pressure unit much used now in barometric work is the 'bar', which is defined as a pressure of one million dynes per square centimetre. Sometimes, however, the 'bar' is used to mean one dyne per square centimetre.

Measurements of pressure may be divided roughly into two classes: (1) the pressure is balanced against the gravitational force on a known mass; (2) the pressure is measured by its effect on some physical property of a body. The first may be termed an 'absolute' measurement, as the pressure may be calculated as a force per unit area by direct measurement; the other method is usually a secondary determination, as the apparatus must first be standardized, using known pressures. The most common form of the first type is that in which a liquid column of known density is supported by the pressure. As the pressure is hydrostatic, the height only of the column need be measured. Another form is that in which the pressure supports a weight

upon a small piston; the accurate measurement of the piston and weights gives the pressure directly. The secondary class of manometer usually depends upon the elastic deformation of a body; spiral springs or metallic diaphragms are usually used; these manometers are first standardized against absolute manometers.

**Practical Classification.** For practical purposes the above division of pressure gauges is not a suitable plan of treatment; the subject can more efficiently be treated as

- (1) Measurement of normal pressures
- (2) Measurements of low and varying pressures
- (3) Measurement of high pressures

**Normal Pressures.** Normal pressures may be taken to mean pressures approximately between 10 and 1,000 mm. of mercury. For the measurement of such pressures open liquid column manometers may be employed. The manometer is of the U-shaped pattern (Fig. 56 (XII)), and is partly filled with the working liquid; one limb is connected to the source of pressure, the other is left open. This often means that the second surface is under



FIG. 56 (XII)

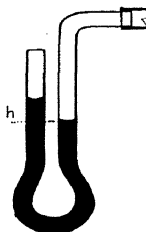


FIG. 57 (XII)

atmospheric pressure and the reading of a standard barometer must be added to the difference in pressure between the manometer limbs. In any case the pressure on the open limb must be known, the observed reading being only that of a pressure difference. For accurate reading of surface level, the manometer should be constructed to have the limbs as close as possible. The strict U-shape is therefore modified, as shown in Fig. 57 (XII); the tube should be of fairly uniform bore, about 7 mm. in diameter. Smaller diameters are very often used, in which case capillary effects, owing to lack of uniformity, may cause inaccuracy.

**Manometric Liquid.** For small pressure differences, a liquid of low density had best be used. In technical practice water is commonly employed. This liquid is convenient for various reasons, and its density is known; for accurate work, however, it is not to be recommended owing to its high and easily variable surface tension and its high vapour pressure. Olive oil has a low and constant surface tension and a negligible vapour pressure; fluess oil has similar advantages and may be recommended. The densities of these liquids at the working temperature can be determined by means of the pycnometer.

For larger pressures mercury must be employed; its high density reduces the apparatus to working dimensions, and it possesses the further advantage


of being non-absorbent to gases. Its high surface tension, with its sensitiveness to impurities, gaseous or otherwise, is a disadvantage. In accurate work the capillary depression must be allowed for. The height of the meniscus is variable and must be measured as well as the diameter of the tube. The following table from Kohlrausch gives the amount of the correction which has to be added to the height for various sizes of tubes.

CAPILLARY DEPRESSION OF MERCURY

Diameter of tube in mm.	Heights of meniscus in mm.							
	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
4	0.83	1.22	1.54	1.98	2.37	—	—	—
5	0.47	0.65	0.86	1.19	1.45	1.8	—	—
6	0.27	0.41	0.56	0.78	0.98	1.21	1.43	—
7	0.18	0.28	0.40	0.53	0.67	0.82	0.97	1.13
8	—	0.20	0.29	0.38	0.46	0.56	0.65	0.77
9	—	0.15	0.21	0.28	0.33	0.40	0.46	0.52
10	—	—	0.15	0.20	0.25	0.29	0.33	0.37
11	—	—	0.10	0.14	0.18	0.21	0.24	0.27

**Setting and Reading the Manometer.** For correct reading the manometer must be erected in a vertical position. Any deviation from the vertical involves an error, proportional to the cosine of the displacement angle; accordingly, a plumb line should be employed. To measure the difference in height of the liquid columns use of the cathetometer is customary. The method of using this instrument was described in an earlier chapter. The possibility of error in this measurement is great owing to possible bad adjustment of the instrument and parallax errors. It is better to have the scale in contact with the glass of the tube. A millimetre scale etched on the glass of the manometer tube is probably the ideal method; the reading telescope, if used, need not then be adjusted exactly. The use of a mirror scale is also to be recommended; the manometer is clamped to the scale, which is set vertically; in reading the level of the meniscus the eye is so placed that the reflection in the scale is in line with the meniscus itself; errors due to parallax are then impossible. Metal scales clamped alongside the manometer and provided with a vernier adjustment are also used. In accurate work, whatever scale is used, its graduations should be corrected for the difference in temperature between that during the experiment and that at which graduation was made.

A slight variation on this type of manometer is sometimes used. A wide-open tube is bent on itself as shown in Fig. 58 (XII). The lower end of the long limb dips into a mercury reservoir; the other end is connected to the pressure source.


 FIG. 58 (XII)

A barometer is placed in the same reservoir and the difference in level is measured by means of a scale placed behind them.

**Vacuum Manometers.** Atmospheric pressure is always varying to a small extent, so in some cases comparison with this pressure is not advisable. Manometers are made independent of the atmosphere by having a vacuous space above the mercury column, thus giving a direct pressure reading. One end of the manometer is connected to the pressure source and the other is sealed so as to enclose a perfect vacuum (Fig. 59 (XII) ). This is rather a difficult process ; usually the closed tube is boiled out with mercury for some time till all air is expelled ; the usual test for a good vacuum is the sharpness

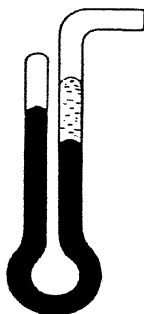


FIG. 59 (XII)

FIG. 60 (XII)



FIG. 61 (XII)

of the sound emitted when the mercury is allowed to run back and strike the end of the tube (click test) ; the length of the closed arm is fixed according to the pressures to be measured. When pressures up to hundreds of millimetres are being measured the closed limb is correspondingly long ; the boiling out of such tubes is very difficult, so another method may be employed. Instead of sealing the end of the manometer, it is provided with a glass tap (Fig. 60 (XII) ) ; below the tap is a small bulb connected with the main tube by a narrow constriction. The air is driven out through the top

by tilting the tube or applying pressure, thus allowing the mercury to rise through the tap. The tap is then closed; as the mercury sinks the thread is broken in the constriction to allow a little to remain in the bulb; this provides an airtight stop on the manometer tube.

**The Barometer.** A great number of pressure measurements are dependent on the pressure of the atmosphere; the instrument used for this measurement is known as the barometer; the common form of mercury barometer is a particular instance of the vacuum manometer already mentioned. The atmospheric pressure is balanced against that of a column of mercury standing vertically in a tube. A diagram of Fortin's Standard Barometer is appended (Fig. 61 (XII)). The barometer is fitted with an adjustment for the level of the mercury in the reservoir and with a vernier attachment for reading the height accurately. In accurate work a temperature correction must be introduced and a correction for the capillary depression of the mercury in the tube.

**Aneroid Barometer** This instrument is not capable of the accuracy of the mercury barometer. Its operation depends upon the movement of a thin metallic membrane under a pressure difference on its faces (Fig. 62 (XII)). This movement is then magnified for reading purposes by a lever system.

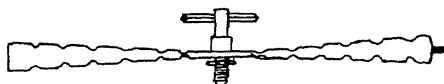


FIG. 62 (XII)

The fundamental feature is the 'vacuum box' formed by two corrugated German silver discs and completely evacuated of air; the lower diaphragm is fixed, but the upper is capable of responding to pressure. The calibration of the aneroid barometer is carried out by a standard barometer.

**Barometer Corrections for Temperature.** Atmospheric pressure is generally recorded in millimetres of mercury corrected to 0°. The correction from temperature of reading  $t$  to 0° can be made by the formula

$$H_0 = \frac{1 + \alpha t}{1 + \alpha_1 t} H = \left( 1 - \frac{(\alpha_1 - \alpha)t}{1 + \alpha_1 t} \right) H$$

where  $H$  is the height of the barometer at temp.  $t^\circ$   
and  $H_0$   $0^\circ$

$\alpha = 0.0000184$ , linear coefficient of expansion of brass

$\alpha_1 = 0.0001816$ , mean cubical coefficient of expansion of mercury at laboratory temperature

The value at 0° can also be made by means of the formulae:

$$H_0 = H - 0.000172 Ht \text{ where the scale is on glass}$$

$$H_0 = H - 0.000161 Ht \text{ where the scale is on brass}$$

The values of  $0.000172 Ht$  at different temperatures and pressures is given in Table A. The corresponding values for  $0.000161 Ht$  are given in Table B.

For pressures outside the range recorded the required values can be interpolated.



TABLE A

Reading of height of mercury (glass scale)

	730		750		760
12	1.5	1.55	1.55	1.55	1.6
13	1.65	1.65	1.7	1.7	1.7
14	1.75	1.8	1.8	1.85	1.85
15	1.9	1.9	1.95	1.95	2.0
16	2.0	2.05	2.05	2.1	2.1
17	2.15	2.15	2.2	2.2	2.25
18	2.25	2.3	2.3	2.35	2.4
19	2.4	2.4	2.45	2.5	2.5
20	2.5	2.55	2.55	2.6	2.65
21	2.65	2.65	2.7	2.75	2.75
22	2.75	2.8	2.85	2.9	2.9
23	2.9	2.95	2.95	3.0	3.05

TABLE B

Reading of height of mercury (brass scale)

<i>t</i>	730	740	750	760	770
12	1.4	1.45	1.45	1.45	1.5
13	1.55	1.55	1.55	1.6	1.6
14	1.65	1.65	1.7	1.7	1.75
15	1.75	1.8	1.8	1.85	1.85
16	1.9	1.9	1.95	1.95	2.0
17	2.0	2.05	2.05	2.1	2.1
18	2.1	2.15	2.15	2.2	2.25
19	2.25	2.25	2.3	2.3	2.35
20	2.35	2.4	2.4	2.45	2.5
21	2.45	2.5	2.55	2.55	2.6
22	2.6	2.6	2.65	2.7	2.75
23	2.7	2.75	2.75	2.8	2.85

**Barometer Corrections for Latitude and Height above Sea-level.**

It is general to take ' $g$ ' at sea-level and  $45^\circ$  as the standard value for gravity.

The barometer correction for latitude is  $\frac{H_0}{760}x$ . This has to be added to the temperature barometric reading  $H_0$  for latitudes from  $45^\circ$  to  $90^\circ$  and subtracted between latitudes  $0$  to  $45^\circ$ . The 'gravity correction' of the barometer for heights above sea-levels is approximately 0.13 mm. of mercury for every 1,000 metres above sea-level. This correction is subtracted from the observed reading.<sup>1</sup>

	0°	10°	20°	30°	40°
Latitude	90°	80°	70°	60°	50°
	1.97		1.51	0.98	0.34

<sup>1</sup> For detailed table, see Kaye and Laby, *Phys. and Chem. Constants* (Longmans, Green & Co.), London.

The capillary corrections of the mercury column are negligible for tubes of greater diameter than 3 mm. The corrections in table are added to the heights for various diameters of glass tubing and meniscus heights.

Bore of Tube	Height of Meniscus (mm.)			
	1	1.2	1.6	1.8
mm.	mm.	mm.	mm.	mm.
8	0.38	0.46	0.56	0.77
10	0.20	0.25	0.29	0.33
12	0.10	0.13	0.15	0.18
14	—	0.06	0.08	0.11

**Barograph.** For the continuous recording of the variation of pressure with time an instrument known as the barograph is used. This is essentially an aneroid barometer fitted with a clockwork device so that a trace is made on squared paper, stretched on a uniformly rotating drum, by means of a stylus. The result is a time-pressure curve on the squared paper. The instrument is illustrated in Fig. 63 (XII).

f  
gh

FIG. 63 (XII)

**Micro-manometers.** Where very small differences of pressure are to be read, both pressures being nearly atmospheric, a special type of gauge is necessary. Increased accuracy is attained by magnification of the effect due to the pressure, i.e. the displacement of liquid columns, the movements of diaphragms, &c. The simplest method of magnifying the difference in height of liquid columns is to construct one of the tubes at an angle to the horizontal and to measure the distance moved along the tube; the value of the angle being known, the actual change in height = length  $\times$  sin  $\alpha$ . The sensitiveness of this type of manometer insists on accurate temperature control; the use of narrow tubes is necessary owing to the large meniscus presented in the vertical tube.

**Compensated Micromanometer.** Roberts has described a micro-manometer capable of great accuracy (Fig. 64 (XII)). The two limbs A and A<sub>1</sub> of a U-tube are connected by a tube of finer bore B, containing an index bubble of air C. A slight change in pressure, causing a transference of liquid from A to A<sub>1</sub> or vice versa, will cause a very appreciable motion of the liquid in the fine-bore tube B. The bubble acts practically as a piston and normally no fluid will pass it. Hence the motion of the bubble along B varies as the change in pressure. The length of the index bubble C should be approximately equal to the distance between the centres of the limbs A and A<sub>1</sub>; it will then be found that the gauge is practically indifferent to

changes of position or level, as the effect of the air bubble, while in the lower horizontal tube, will counteract any change of level of the limbs A and A<sub>1</sub>. The sensitiveness of the gauge depends on the ratio between the diameters

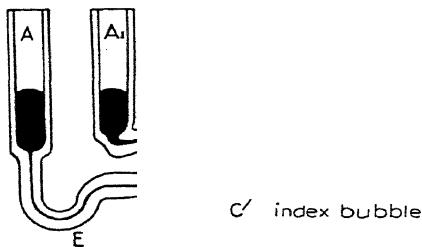


FIG. 64 (XII)

of A and A<sub>1</sub>, and B, and also on the liquid used; for the most delicate results, alcohol or ether should be used. If A and A<sub>1</sub> are 10 mm. in diameter, and B is 0.5 mm., the magnification is 400 to 1.

**Diaphragm Micromanometer.** In this apparatus the pressure is measured by the movement of a thin diaphragm; delicate reading is effected

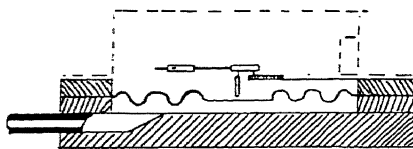


FIG. 65 (XII)

by the use of an optical lever arrangement; the apparatus is represented in Fig. 65 (XII). The motion of the diaphragm is communicated to a mirror mounted on three pins forming an optical lever; the reflected ray is received on a screen fixed at a distance; the

pressures will be proportional to the deflections. Other diaphragm gauges make use of the Fizeau interference method instead of the optical lever for delicate measurements.

**A Sensitive Direct Reading Manometer.** A manometer accurate to 0.001 mm. of mercury has been described by Melville.<sup>1</sup> It consists of a small inverted glass cup (c) floating in mercury as shown in Fig. 66 (XII), *a*. The simple theory is as follows. Let the pressures of gas on the outside and inside of the cup be identical, the cup will then sink into the mercury until the weight of liquid displaced is equal to the weight of the cup. If the pressure is now increased on the outside of the cup by  $\Delta p$  the total force exerted downwards on the cup is proportional to  $\eta r^2 \cdot \Delta p$ , where  $r$  is the radius of the cup. This will result in the cup sinking further into the mercury by a distance  $\Delta x$ , the weight of mercury displaced being equal to  $\Delta x 2\pi r t \rho$ , where  $t$  is the thickness of the cup and  $\rho$  the density of mercury (in addition the levels of the mercury outside and inside the cup change, but this motion is small compared with the motion of the cup in this particular case and is therefore neglected in the simple theory). For equilibrium, then,

$$\Delta p \cdot \pi r^2 = K \cdot \Delta x \cdot 2\pi r t \rho$$

<sup>1</sup> *J. Chem. Soc.*, 1931, 139, 2509.

where  $K$  is a constant depending only on the units used to express  $\Delta p$ . The sensitivity  $\frac{\Delta x}{\Delta p}$  is thus given by  $\frac{\Delta x}{\Delta p} = \frac{r}{2Kt\rho}$ , and in order to make this large,  $r$  must be large and  $t$  small. Calculation showed that if  $r = 1$  cm.,  $t = 10^{-2}$  cm., and the smallest value of  $x$  which can be detected is  $10^{-3}$  cm. (by means of a microscope fitted with an eye-piece scale), the required sensitivity could be reached.

Two different forms of the manometer were constructed as shown in Fig. 66 (XII), *a* and *b*. The glass cups were made from 1-cm. tube by drawing and blowing it simultaneously. The tubing was then cut into convenient lengths by covering the selected parts with paraffin wax, drawing

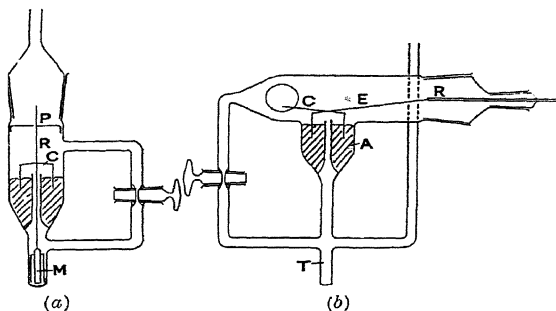


FIG. 66 (XII)

a furrow in the wax with a fine steel point, and etching through with hydrofluoric acid. For practical purposes, the limit to the thickness was about  $10^{-2}$  cm. The cup was attached to the glass rod (R) as shown in Fig. 66 (XII), *a*. At the lower end of the rod a small tube (M) filled with mercury was fused on in order to sink the cup well into the mercury and bring the centre of mass of the floating system below the surface of the mercury. This tube moved in a glass guide, and a guide (P) of platinum wire or foil served at the upper end of the rod. The large ground joint facilitated the adjustment and removal of the cup, and the tap allowed the manometer to be used differentially.

Fig. 66 (XII), *b*, shows a different arrangement in the guides for the cup. In this case the cup was supported by two thin glass fibres (E) so that vertical motion could easily take place, whereas horizontal movement was prevented. These were attached to a glass rod (R), which in turn was fused to one half of a ground joint as shown. The large joint was necessary for the insertion and removal of the cup. The small joint was made slightly eccentric with respect to the large one so that the cup could be accurately adjusted when the manometer was evacuated. The motion of the cup was observed by means of a fine glass pointer (C). A magnification of motion can be obtained by the supporting fibres. The side tube (T) prevented the blocking of the tube leading to the apparatus in the event of mercury being forced out of A by sudden pressure changes in the apparatus. The absence of glass and metal guides in this form eliminates to a large extent any tendency to stick.

**Impulsive Pressures.** The piezo-electric method of Thomson gives the most accurate results for this kind of transitory pressure. The technique is difficult, as it involves the use of a cathode ray oscillograph. A simpler method has been devised by Dowling and McHenry. The principle of the method is simple. A steel diaphragm is exposed to the pressure wave and closes an electrical contact, provided that the pressure has attained a certain predetermined minimum value. The occurrence and duration of the contact is indicated electrically. Means are provided for adjusting beforehand the pressure of response.

## HIGH-PRESSURE MEASUREMENT

**Mercury Columns.** The standard method in high-pressure measurement is the use of high mercury columns. A mercury column is generally used by makers of pressure gauges as a standard of reference up to 20–30 atm. In construction there is no fundamental difference from the normal pressure columns. The height and unwieldy nature of the column, however, necessitate great care in construction. Temperature variations throughout the column are difficult to obviate or correct for, and may cause serious errors. In most cases it is not convenient to erect such columns for high pressures. A modified mercury gauge for such pressures has been constructed by Kammerlingh Onnes. The principle of the gauge may be deduced from

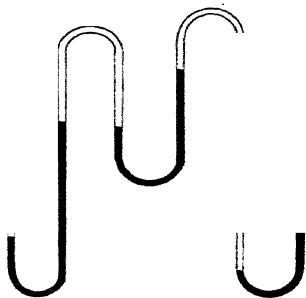


FIG. 67 (XII)

Fig. 67 (XII). The pressure is applied to the left-hand tube, forcing the mercury up in the right arm of the first tube; this compresses the air in the intermediate space between the mercury columns, causing the mercury to rise in the right-hand tube of the second U-tube, and so on to the end of the series. The initial pressure is then obtained by adding the differences of pressure along the battery. In practice compressed air is admitted to the intermediate spaces to utilize the full range of each U-tube (about 4 atm.). This does not affect the use of the instrument. A correction must be applied

for the weight of the air column in each tube. Fig. 68 (XII) is a diagram of the instrument omitting most of the intervening tubes. The whole gauge contains twenty-four intervening U-tubes, such as shown, the first siphon (on left) of the same diameter throughout for the measurement of fractions of an atmosphere, and a short U-tube (at the pressure end) for adjustments to 2 atm. A tube is connected with a cylinder of compressed air, with a Bourdon gauge, and with the unknown pressure, through different stopcocks. The gauge indicates the approximate pressure to which the manometer must be adjusted before the cock connecting with the latter is opened. The heights of the columns are read off on graduated rods suspended between the columns, the temperature of each being determined by a thermometer beside it.

**Closed Mercury Column Manometer.** In this manometer the pres-

sure is measured by the amount of compression of a gas; the mercury is used to indicate the volume of the gas. This gauge is not very accurate over a large range, but with careful calibration initially, it may be made a reliable primary manometer.

The general form of such manometers is indicated in Fig. 69 (XII). It consists of a strong vessel of iron or steel partly filled with mercury and having a connexion to the pressure apparatus. In this is fixed a glass vessel B, wide in the lower portion, the upper being a thick-walled graduated tube. At the bottom of the wide portion is a small, bent-up tube open to

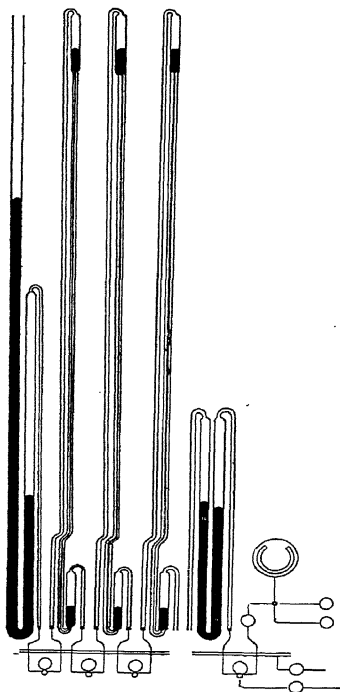


FIG. 68 (XII)

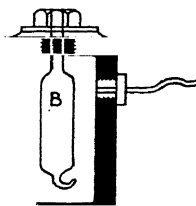


FIG. 69 (XII)

the mercury. The volume of the whole glass vessel must be known and the volume between each graduation and the tip of the narrow tube; these may be determined by weighing with mercury. The manometer is best filled with dry hydrogen, as this gas deviates least from Boyle's Law. When pressure is applied the mercury is forced into the bulb. No reading can be taken until the mercury reaches the narrow graduated tube. The volumes of the bulb and tube must be selected so that the mercury will be on the scale over the required pressure range.

The volume occupied at the original atmospheric pressure being known, the volume at 760 mm. may be calculated. Let this equal  $V_0$ .

Then for the pure hydrogen the formula

$$P = \frac{1}{\frac{v}{V_0} - 0.000662} \text{ atm.}$$

gives the pressure for any volume  $V$ .

The temperature effect is not easily corrected for, so it is more convenient to work altogether in a thermostat at a constant temperature. The hydrostatic pressure of the mercury column must be added to that obtained above.

**Loaded Piston Primary Manometer.** This type of manometer for measuring high pressures appeals through its direct measurement. The unknown pressure is balanced by weights acting on a piston fitting closely into a cylinder. By making the dimensions of the piston small, the weights

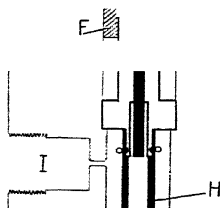


FIG. 70 (XII)

FIG. 71 (XII)



FIG. 72 (XII)

may be of ordinary dimensions and yet balance a pressure of tons per square inch. The difficulties in the method are the construction of a small piston and cylinder free from friction and leakage and the accurate measurement of the diameter. Amagat used this type of manometer in his compressibility determinations. Amagat's instrument was found to leak at very high pres-

tures. Bridgeman has constructed a similar instrument by which pressures up to 6,800 kilograms per square centimetre may be measured. The cylinder and piston are shown in Fig. 70 (XII). In Fig. 71 (XII) they are shown in place in a large steel block, and in Fig. 72 (XII) the dimensions are given. The thrust on the piston P (Fig. 70 (XII)) is taken by the large cylindrical rod A, joined to the piston. A terminates in a hardened steel point B, on which the weights are hung by a stirrup supporting the scale pan beneath the steel block.

To diminish the friction between the piston and cylinder, the former was kept in slow oscillatory motion through  $30^\circ$  by means of a small motor. A very viscous mixture of molasses and glycerine was used to transmit the pressure in the cylinder; this prevented any leak between piston and cylinder even at high pressures.

The cylinder used was made from about 1.25 per cent C tool-steel; the piston was a piece of 0.0625 inch (1.59 mm.) drill rod. To measure the diameter of the piston and cylinder directly was not practicable owing to their size; accordingly, a larger piston 0.25 inch diameter was constructed to fit another cylinder and the two instruments used simultaneously to measure the same pressure. The diameter of the larger piston was measured accurately with a micrometer and the diameter of the smaller one calculated.

A somewhat similar high-pressure instrument has been used in the National Physical Laboratory. Instead of using one very small piston, two pistons of very nearly equal diameter are used at opposite ends of a cylinder and the resultant force measured. This force is small as the pistons are very nearly equal in area; knowing the difference in area and the weight, the pressure in the cylinder may be calculated. Thus, in an instrument where the difference in area is 0.01304 square inch and the load 29.21 lb., the pressure in the cylinder is 1 ton per square inch.

**High-pressure Secondary Manometers.** The majority of such instruments depend upon the elastic deformation of some metal body. They must be calibrated by comparison with a reliable primary gauge. An important 'hysteresis' defect in all such gauges is that the calibration curve as the pressure increases does not coincide with the same curve as the pressure decreases. Each instrument is constructed to read over a certain range; care must be taken not to reach the elastic limit of the material, since this will result in a permanent deformation of the metal part.

**Bourdon Tube Gauge.** The most common form of such manometers is the Bourdon tube gauge. These gauges are constructed to read pressure ranges both high and low. The gauge is shown in Fig. 73 (XII). The pressure is applied to the inside of a tube of metal filled with oil; for low pressures the tube is made of German silver and for high pressures of steel. The tube is usually bent into the form of an arc. When the pressure is applied the arc tends to stretch and, one end being fixed to the casing, the free end is used to record the movement by means of a gear system connecting with a pointer. A small

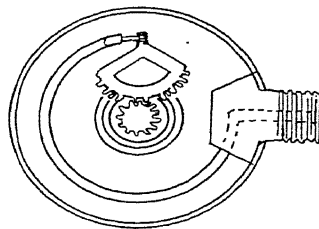


FIG. 73 (XII)



retarding hair-spring is used to prevent free movement of the pointer. The reading may be sensitized by combining the pointer with an optical system, but, in general, it is not advisable to trust the accuracy too far.

Bourdon glass gauges are easily constructed and are suitable for the measurement of the pressure of corrosive gases. The gauge quickly records changes of pressure and they can be obtained for any range of pressure from vacuum up to 10 or 12 tons per square inch. With small pressure readings it would be necessary to calibrate the scale at different temperatures and to make temperature correction tables.

Norrish in a study of the photochemical union of hydrogen and chlorine and other gases employs a Simple Bourdon gauge in his apparatus. His gauge is efficient either as a direct recording instrument for small pressure changes of from 1 mm. to 50 mm. or as a 'null' instrument for recording pressure up to 1 atm. It is made by blowing a thin glass bulb of about 7 cm. capacity, attaching a style of glass about 20 cm. long and then heating in a flame and drawing in one side to a horse-shoe shape. Variations of pressure inside the gauge caused movement of the style, the shadow of which was focused on a translucent scale and observed through a magnifying-glass. The gauge was calibrated by measuring small pressure differences between the inside and outside directly on vertical mercury manometers, using a travelling telescope. It was found in one particular instrument that a deflexion of the gauge pointer by 1 mm. corresponded to a pressure change of 700 mm., the probable error on the determination of a pressure change of the order of 2 mm. being not greater than 2 per cent.

**Resistance Manometers.** This type of manometer depends upon the change in resistance of a metal when subjected to pressure. A sensitive resistance bridge must be used to measure the change. Resistance gauges are found to show no 'hysteresis' effect for increasing or decreasing pressures; in this respect they are superior to elastic gauges. The metals used in this method are mercury, platinum and 'manganin'. Bridgman has constructed a mercury resistance manometer, which acts very well as a secondary manometer. The mercury is enclosed in a U-tube capillary, the electrodes dipping into two cups at either end. A straight capillary tube is also used. The resistance was measured by means of a Carey-Foster bridge and calibrated with the piston primary manometer already described. In later papers the same worker describes the measurement of pressures up to 20,000 atm. with resistance gauges.

**Crusher Gauge.** This gauge is used in technical practice for single high-pressure measurements. The pressure is allowed to act on a piston which permanently deforms a small metal cylinder; the pressure is then read from a pressure-deformation curve previously obtained with similar cylinders in a testing machine at known pressures. The gauge is used in determining the explosive pressure in the breech chamber of a gun.

## SECTION 9: VACUUM MEASURING INSTRUMENTS

The accurate measurement of low pressures has been accomplished by a variety of instruments based on different properties of gases at low pressures. Boyle's Law, heat conductivity, ionization, and viscosity, are some of the properties used in these measurements. In the simplest type, the balancing of mercury columns, accuracy is obtained by use of an optical method of measurement. This is the method applied by Rayleigh to the measurement of low pressure.

**U-Tube Manometer.** The usual instrument is filled with mercury, and can be read to 0.2 mm. with the eye. Modifications can be made, e.g. see Carver, *J. Amer. Chem. Soc.*, 1923, 45, 59.

**The Butyl Phthalate Gauge.**<sup>1</sup> High boiling-point organic liquids generally contain traces of solvents and water vapour and air. When such liquids are placed in a U-tube having one limb closed it is impossible to displace the liquid from the closed end by applying a vacuum to the other end of the U-tube, that is, the open end. The butyl phthalate gauge has been constructed with a small pumping system at the closed end to keep up a reference vacuum. The phthalate manometer has a butyl phthalate condensation pump, a vessel for storage of gases and a Sprengel tube. This type of manometer is difficult to use and needs very careful manipulation. It must be exhausted for an hour before use.<sup>2</sup> Palkin<sup>3</sup> describes a gauge using hydrocarbon oil and which does not require a condensation pump. Spiezon oils (*q.v.*) have also been used in gauges.

**Rayleigh's Manometer.** In this manometer the unknown low pressure is compared with that in an extremely good vacuum by means of mercury columns. The essential parts of the manometer are shown in Fig. 74 (XII). Two glass bulbs (B) are connected by tubes C to a high vacuum and to the unknown pressure respectively. Two glass points, connected to a T-piece forming the upper ends of a barometer A, are sealed into the bulbs. The mercury level in the bulbs can be varied by the reservoir D (Fig. 75 (XII)). A mirror is fixed vertically on top of the bulbs at M. The whole is cemented to a vertical board, itself connected to a levelling table, which can be tilted about a horizontal axis by a levelling screw J. At first the mercury levels are brought just in contact with the glass points by means of D. When the difference in pressure is established, one surface leaves the point and is brought back again by tilting the whole apparatus by means of the screw J. The rotation of the mirror is observed by means of a telescope and millimetre scale and gives the value of the pressure difference. According to Rayleigh this gauge can be used to read pressures between 1.5 mm. and  $1 \times 10^{-3}$  mm. of mercury.

<sup>1</sup> Reilly, *Distillation* (Methuen), 1936.

<sup>2</sup> Hickman, *J. Amer. Chem. Soc.*, 1930, 52, 4714.

<sup>3</sup> *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 434.

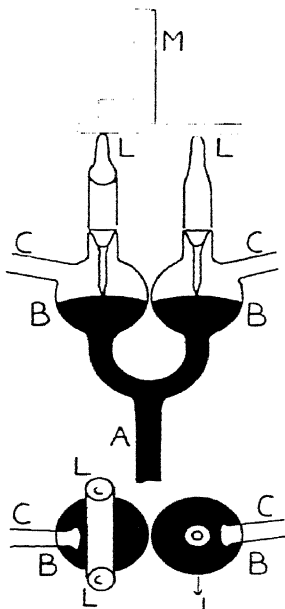


FIG. 74 (XII)

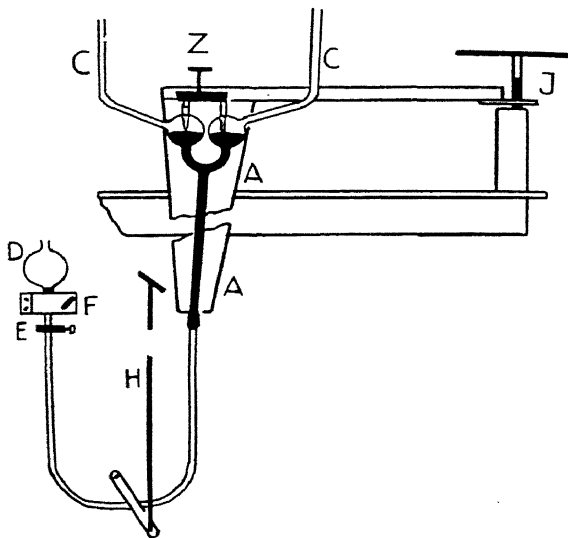


FIG. 75 (XII)

**Optical Lever Manometer.** A manometer of this type has been described by Shrader and Ryder<sup>1</sup> for the measurement of pressures between

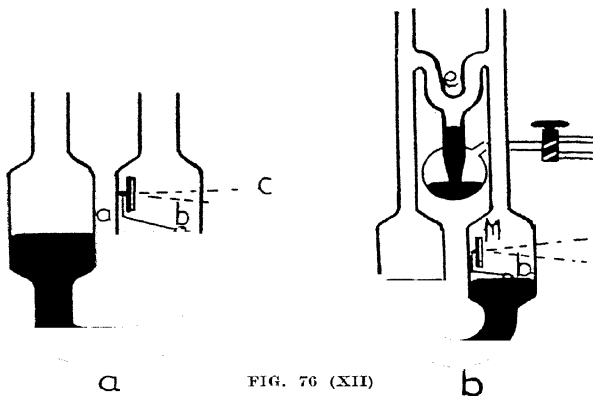


FIG. 76 (XII)

0.001 mm. and 3 or 4 mm. of mercury. The manometer is especially useful in recording rapid variations in pressure. The principle of the gauge is shown in Figs 76 (XII) *a* and *b*. It consists of a mercury U-tube mano-

<sup>1</sup> *Physical Rev.*, 1919, 13, 321.

The gauge is claimed to be sensitive to  $10^{-3}$  mm. of mercury.

The sensitivity of the gauge depends on the ratio of the volumes  $V$  and  $v$ . The gauge can only be used for indicating the pressure of 'permanent' gases; investigations by Rayleigh and Scheel and Heuse have shown that Boyle's Law holds accurately for these gases at low pressures. It cannot, of course, be used for the non-permanent gases or for measurements of vapour pressure, owing to the non-applicability of Boyle's Law.

In making a reading the reservoir is raised so that the mercury rises in V and E, forcing the gas into the capillary. The pressure on the gas in the capillary is then equal to the height of the mercury column  $l$ , plus the small unknown pressure. The latter is then calculated from Boyle's Law.

If the mercury in the by-pass capillary is just brought to the tip of  $a$ , then  $l$  is also the length of the gas column in  $a$ . The low pressure  $P$  is then equal to  $\frac{(A \cdot l)l}{V}$  or  $\frac{Al^2}{V}$  where  $A$  is the volume of gas per unit length. The pressure is therefore proportional to the square of the observed height; also it is

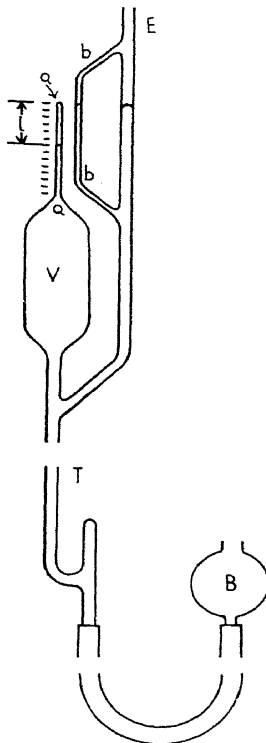


FIG. 77 (XII)

seen that the sensitivity depends upon the ratio  $\frac{A}{V}$ ; practical considerations, however, prevent this ratio from being made very small. The maximum value for  $V$  may be fixed at 500 ml., and the minimum diameter of the capillary at 0.5 mm. For very sensitive working with dimensions exceeding these limits a special design of apparatus is necessary.

The form of the gauge is outlined in the accompanying sketch (Fig. 78 (XII)). The apparatus is dried thoroughly by allowing phosphorus pentoxide to stand in the reservoir  $R$  for 2 days. After the drying agent has been removed the reservoir is about three-quarters filled with pure dry mercury. The reservoir is next evacuated by means of a water pump connected to one of the nozzles of the two-way tap  $A$ , and the vessel whose internal pressure has to be measured is connected to the tap  $B$ .

To make a measurement, the two-way tap  $A$  is turned so that a slow inlet of air to  $R$  occurs. The increase of pressure in  $R$  causes the mercury to rise in the vertical tube  $T$ . In its rise the mercury isolates a quantity of gas in the bulb  $V$ . The volume of the bulb is known and at the moment of isolation the gas in  $V$  is under the same pressure ( $p$ ) as that in the vessel whose pressure is being measured. Further rise of the mercury column compresses the gas in  $V$  till it is all contained in the graduated capillary tube  $t$ . This tube has a flat end and is of known cross section, hence the volume ( $v$ ) of any observed length is known. The pressure ( $P$ ) to which this compressed gas is subjected is measured by the difference of the mercury levels in the tubes  $t$  and  $F$ . To avoid any errors due to capillarity or to personal equation the tubes  $t$  and  $F$  are made of the same bore.

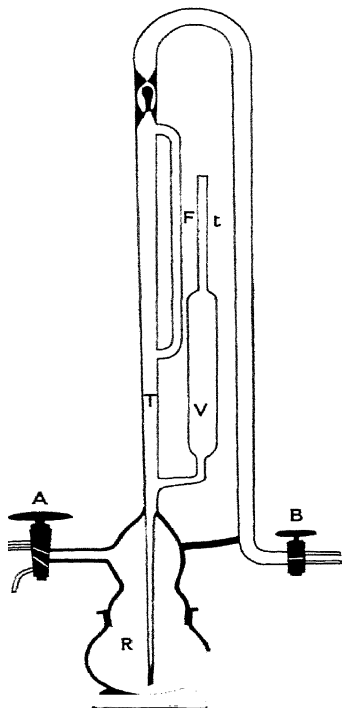


FIG. 78 (XII)

In practice it is customary to adjust the head of the pressure column in  $F$  to the top of the tube  $t$ . Under this condition, for any fixed value of  $v$  there will be always the same value for  $P$  and hence the same value for  $p$ . The graduations on  $t$  may therefore read, instead of volumes, the values of the original pressures  $p$ , and the scale provided with the instrument is graduated in this way.

When a fresh reading is required the tap  $A$  is turned to connect with the water pump. The pressure in  $R$  is reduced and the mercury in  $T$  falls. When the opening from  $V$  is clear, the gas in  $V$  is at the new pressure of the vessel to be measured and this is determined as already described.

Since water vapour and carbon dioxide do not follow Boyle's Law, it is advisable to remove these gases by interposing between B and the vessel to be tested U-tubes containing (a) phosphorus pentoxide and (b) soda lime.

In some forms of apparatus the rise and fall of mercury is effected by raising and lowering a bulb of mercury connected by rubber tubing to the lower end of the tube T.

A valve in the upper part of T closes with any undue rise of the mercury column and prevents mercury passing over into the test vessel.

A direct reading manometer (with pressures of the order of 0.001 mm.) has been described by Trombe.<sup>1</sup>

**A Cut-off for High Vacuum Work.** A practical point in connexion with the use of high vacuum pumps is the need for a simple cut-off that will 'let down' the low vacuum side without also destroying the high vacuum on the other side. The cut-off shown in Fig. 79 (XII) was primarily designed by Ditchburn<sup>2</sup> to prevent mercury being violently flung into the high vacuum side when an accidental break happened on the low vacuum side. It also enabled gas at atmospheric pressure to be suddenly admitted to the low-vacuum side without disturbing the high vacuum. The following points of design are important:

- (1) The taper at H where the two ground surfaces come into contact must be fairly sharp, to avoid sticking.
- (2) If the float should stick slightly and then fall suddenly it would smash itself on the bottom of the tube T. To avoid this the connecting tube B is led out in such a way as always to leave some mercury in the bottom of T.
- (3) The bulge (in the float) at C is required to ensure that it always rises and falls vertically. The cut-off shown in Fig. 79 (XII) does not protect the low vacuum against a break on the high vacuum side. With modifications the apparatus can be altered to safeguard the vacuum on both sides.

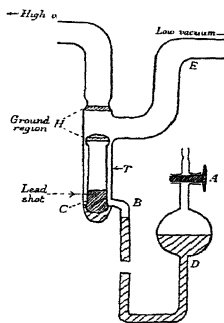


FIG. 79 (XII)

If it is desired to admit air at atmospheric pressure to the low vacuum side without affecting the high vacuum, the design should be modified by transferring the tap from A to D, i.e. it should be placed so that it is always in the mercury. When the valve is merely to be used as a safeguard against a sudden break-down, rough grinding will do. If, however, it is to be used for withstanding a large difference of pressure, for more than a few minutes, good grinding is necessary.

**Elastic Manometers.** Manometers depending upon the elastic deformation of bodies have been used in low-pressure work. Johnson and McIntosh<sup>3</sup> have constructed a gauge of a glass tube bent into a spiral. The walls are made so thin as to be sensitive to very small pressure changes. The reading is obtained by the reflection from a mirror attached to the end of the spiral. Scheel and Heuse<sup>4</sup> have constructed a manometer depending

<sup>1</sup> *Bull. Soc. Chem.*, 1934, I, 408.

<sup>2</sup> *J. Sci. Inst.*, 1931, 8, 267.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1909, 31, 1138.

<sup>4</sup> *Zeitsch. Instrument.*, 1909, 29, 14.

on the deformation of a thin copper membrane. One side of the membrane is connected to the source of pressure and the other to a high vacuum pump. The reading is made by an optical interference method.

**Viscosity Manometers.** In general these manometers may be divided into two classes, 'decrement' and 'torsion'. In the former the rate of decrease of the amplitude of oscillation of a body in the gas is measured; the second type uses the viscous effect of a surface rotating in the gas on an adjacent surface and measures the torque on the latter. Both gauges, of course, depend upon the equations for viscosity in a gas. A quartz fibre manometer of the 'decrement' type was suggested by Langmuir.<sup>1</sup> Haber and Kerschbaum<sup>2</sup> have published a description of this gauge. A thin quartz fibre is fused at the top of a glass bulb and the tube connected to the pressure. The fibre is set in oscillation by gently tapping the glass tube focused by a telescope with a scale at the back of the gauge. Haber has shown that

$$(p\sqrt{M} + a)t = b$$

where  $p$  is the pressure,  $M$  the molecular weight of the gas,  $a$  and  $b$  are constants for the fibre and  $t$  is the interval of time for the amplitude of the oscillations to decrease to half its original value.

A 'torsion' viscosity gauge also suggested by Langmuir has been described by Durham. The rotation of a steel disc by means of an electromagnetic arrangement produces a deflection of a thin mica disc suspended above it by means of a quartz fibre. The rotation is measured, as usual, by the reflection from a mirror attached to the quartz fibre.

**Radiometer Gauges.** The well-known radiometer devised by Crookes has not been found useful for the absolute measurement of gas pressures. A radiometer gauge capable of use as an absolute manometer has been constructed by Knudsen. From theoretical considerations of molecular momentum and heat-transference Knudsen has shown that the force of repulsion per square centimetre,  $K$ , of two parallel surfaces maintained at temperatures  $T$  and  $T'$ , when the distance between them is less than the mean free path of the molecules, varies with pressures and temperatures according to the equation

$$K = \frac{P}{2} \sqrt{\frac{T'}{T}} -$$

which for small differences of temperature may be written

$$P = 4 \frac{KT}{T' - T}$$

dynes per square centimetre.

One form of the apparatus used to measure the repulsive force is shown in Fig. 80 (XII). A glass tube has a narrow tube sealed into it. A rectangular piece is cut from the latter as shown. A fixed fibre suspends a piece of mica in front of this opening. The external tube is heated by means of a water jacket. As the temperature is raised the mica plate is repelled by the bombardment of the faster molecules through the rectangular opening. The

<sup>1</sup> *J. Amer. Chem. Soc.*, 1913, 35, 105.

<sup>2</sup> *Zeitsch. Electrochem.*, 1914, 20, 296.

amount of the repulsion is measured by a microscope. Knudsen's gauge has been elaborated by Shrader and Sherwood.<sup>1</sup>

**Hot Wire Gauge.** Low pressures may also be measured by observing the rate of cooling of a hot wire. The Pirani gauge is of this type (see below). Dr. Shakespear has also devised an instrument of this type.<sup>2</sup> In the form made by the Cambridge Instrument Co., the instrument consists of a Wheatstone bridge system in which the arms are spirals of wire.<sup>3</sup> The temperature to which the arms are raised by a current through the bridge depends on the spacing of the turns, and this property enables it to be used as a measuring device. The mechanical design of the instrument is such that a displacement which is to be measured stretches two spirals that are diametrically opposite in the bridge system and compresses the other pair. Consequently two arms become slightly lower in temperature than the other pair, and the bridge is thrown out of balance, as shown by a galvanometer.

**Pirani Gauge.**<sup>4</sup> The Pirani gauge serves for measurements between 0.1 and 0.0001 mm. It depends on a measurement of the thermal conductivity of the rarefied gas whose pressure is to be measured. It is therefore equally accurate with both vapours and gases. The instrument of Firma E. Leybold's Nachfolger consists of a glass reservoir connected with the apparatus either by a standard joint or fused on. In the reservoir there is a nickel spiral filament. A known current is passed through this filament, which becomes heated to a temperature depending on the conductivity of the surrounding gas. This change in temperature is measured as a change in resistance of the filament which is connected in a bridge circuit. The Pirani gauge indicates variations of pressure almost instantaneously and is therefore generally preferable to the compression manometers in all cases where the gas to be measured is of known composition. The instrument is usually supplied with a calibration curve for air which also holds good for gases of similar molecular weight, e.g. nitrogen, oxygen, carbon dioxide, and argon. Special curves may be made for gases such as hydrogen, helium, &c., whose molecular weight differs considerably from that of air.

**Philips Vacuum Gauge.** The Philips vacuum gauge<sup>5</sup> serves to measure pressures between  $1.5 \times 10^{-3}$  and  $1 \times 10^{-5}$  mm. and the total pressure (gases plus vapours) is indicated (Fig. 81 (XII)).

The Philips vacuum gauge is specially suitable for measuring the vacua during manufacturing processes or in such systems as are continuously

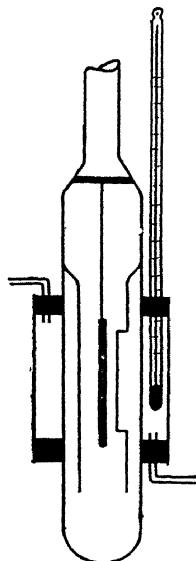


FIG. 80 (XII)

<sup>1</sup> *Physical Rev.*, 1918, 12, 70.

<sup>2</sup> Brit. Patent 219452.

<sup>3</sup> Moss, *J. Sci. Inst.*, 1930, VII, 393.

<sup>4</sup> Firma E. Leybold's Nachfolger of Cologne have supplied the information on this gauge and the other instruments, &c., described to the end of the Chapter. They have also supplied the diagrams from which the electros have been made.

<sup>5</sup> Penning, 'Ein Neues Manometer für niedrige Gasdrucke,' *Physica*, 1937, IV, 2, 71.



evacuated. It is easily operated. The measurement of the vacua is made possible by means of a glow discharge current passing between the electrodes 2 and 3 in the glass reservoir (1) which is connected with the evacuated system. At low working pressures, however, the discharge current would be too small and the striking voltage too high to allow a vacuum measurement on this principle. But in the Philips gauge a permanent magnet (4) is arranged in such a way that the magnetic field is at right angles to the electrical field. This causes the electrons to be deflected and to follow a

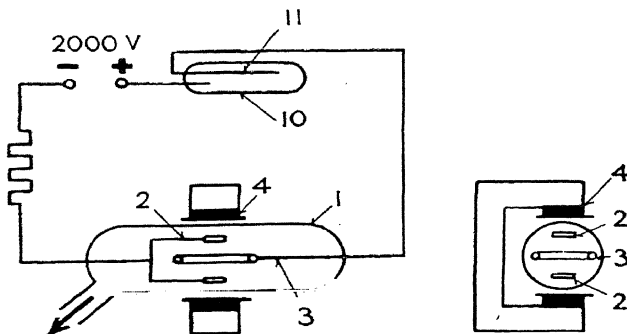


FIG. 81 (XII)  
Circuit Diagram of the Philips Vacuum Gauge

spiral path to the anode, with a consequent increase in the probability of ionization by collision: In this way an appreciable discharge current will flow even at low gas pressures.

A small glow discharge tube (10) with straight cathode (11) acts as indicator. The area of the cathode covered with the glow is a simple indication of the strength of the gas discharge in the tube (1). By calibration the relation between the pressure and the length of the glow discharge may be determined.

The Philips vacuum gauge is operated using mains current.

**Ionization Manometer.** The ionization manometer is the most useful and accurate measuring instrument for pressures below  $1 \times 10^{-3}$  mm. of mercury.

The cathode, grid and anode of the three electrode tubes are normally connected to batteries as shown in Fig. 82 (XII). The electron current is regulated by a resistance  $W$  in the cathode circuit, to a given value as indicated on the milliammeter  $mA$ . No electrons will flow to the grid which is at negative potential and with a perfect vacuum the galvanometer  $G$  would not indicate any current. At the lowest pressures that it is possible to reach there will remain a number of molecules of gas some of which will be ionized by the electron stream. These ions will be collected by the grid and will cause a current to be indicated by the galvo  $G$ . If  $I_+$  is the positive ion current flowing to the grid and  $i_-$  is the electron current flowing to the anode, then

$$p = C \frac{I_+}{i_-}, \text{ where } C \text{ is a constant depending on the nature of the gas.}$$

It is also possible to make the grid positive and to use the anode as the ion collector. This method is preferable on account of its greater sensitivity. The instrument of Firma E. Leybold's Nachfolger may be used for both methods and consists of a three-electrode tube (Telefunken RE11) and an instrument box which may be used for measuring both the anode current and the anode voltage. An A.C. milliammeter reading to 30 ma. is also provided for indicating the current when heating the electrodes by bombardment. For this purpose a thousand volts is provided by a special transformer. In addition to batteries a galvanometer is necessary and to measure a pressure of  $10^{-6}$  mm. this should have a sensitivity of about  $10^{-9}$  amps. (Fig. 82 (XII) ).

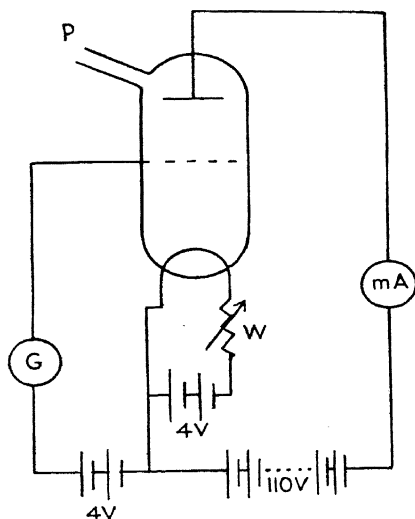


FIG. 82 (XII)  
Circuit Diagram of Ionization Manometer

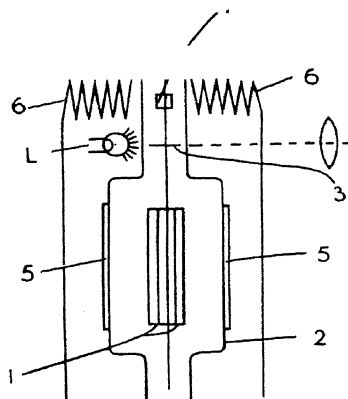


FIG. 83 (XII)

**Gaede's 'Molvacuumeter'.** The 'molvacuumeter' may be employed for measurement of pressures between 10 mm. and  $10^{-7}$  mm. of mercury, and it is possible to use two different methods.

*First Method.* The molvacuumeter (Fig. 83 (XII) ) consists of a very thin metal foil, 1, suspended so as to rotate in a receiver, 2. Special means are provided to ensure that the system revolves only and does not oscillate. Above the foil is a small indicator, 3, and a magnet, 4. At the wall of the receiver there are two heating surfaces, 5 (Fig. 84 (XII) ), arranged con-

centrically to the axis of the metal foil. The molecules emanating from the walls of the receiver and impinging on the foil transfer their energy to the latter. The molecules coming from the heated parts of the walls of the receiver, having a greater speed than those from the cooled parts, a force acts on the foil, 1, having a magnitude determined by its position between the heating surfaces. The equilibrium position occurring thereby is indicated in Fig. 84 (XII).

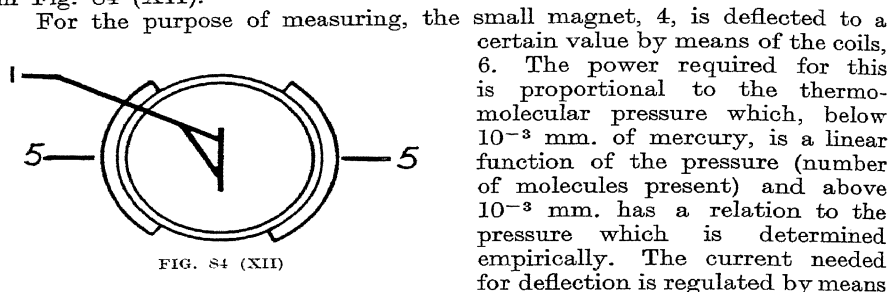


FIG. 84 (XII)

For the purpose of measuring, the small magnet, 4, is deflected to a certain value by means of the coils, 6. The power required for this is proportional to the thermomolecular pressure which, below  $10^{-3}$  mm. of mercury, is a linear function of the pressure (number of molecules present) and above  $10^{-3}$  mm. has a relation to the pressure which is determined empirically. The current needed for deflection is regulated by means of a rotary resistance, on the rotating knob of which the prevailing pressure can be read directly (method 1).

*Second Method.* The reading of the pressure is more accurate if, instead of determining the deflection, the period of oscillation of the system, the relation of which to the pressure is simple, is determined. The period of oscillation is between 2 and 15 seconds. The relative accuracy of this method of measurement is about 1 per cent. It is claimed that such an accuracy has never been reached hitherto with any vacuum measuring instrument.<sup>1</sup>

When measuring, the movement of the indicator, 3, must be observed before a convex scale. The reading may be carried out in daylight.

It may be mentioned that if air is allowed to rush in suddenly the system may be destroyed. To avoid this, a safety valve is usually fitted.

<sup>1</sup> Cf. Gaede, *Zeit. für tech. Physik*, 1934, 12, 664.

## SECTION 10 : ELASTICITY AND TENSILE STRENGTH

The measurement of the constants of elasticity, compressibility and tensile strength is more of a purely physical and commercial than a physico-chemical interest. The bearing of these constants on physico-chemical problems has, so far, been slight and does not warrant a lengthy treatment in this work. Their importance in connexion with problems of structure is being slowly recognized, however, and renders desirable a short description of the methods employed in these measurements. For those desirous of detailed information the references given in the text may be useful.

The evaluation of the different moduli of elasticity, those of volume rigidity and Young's Modulus, in the case of solids, have long been of practical importance, and the experimental methods are commonly known. For laboratory practice the determinations of the latter two constants are well described in Searle's *Experimental Elasticity*. These determinations will therefore not be described here. The determination of the volume modulus or the compressibility is more difficult and is not suited to general laboratory practice. The compressibility of solids is, of course, a very small quantity; hence, very high pressures and very delicate measuring apparatus must be available to carry out such experiments. Measurements of this nature have been carried out at the Geophysical Laboratory of the Carnegie Institution of Washington. The solids are subjected to a hydrostatic pressure in a steel cylinder or bomb (Fig. 85 (XII)). The cylinder is closed at the bottom and fitted at the top with a movable piston; the solid is enclosed and surrounded by a thin liquid which will not solidify or thicken under pressure; this serves to convey the hydrostatic pressure equally to all parts of the solid. If now pressure be applied by forcing the piston downwards and simultaneous readings be taken of (1) the piston displacement and of (2) the resultant hydrostatic pressure in the liquid, the value of the volume change in the contents of the bomb as a function of the pressure will be obtained. It is obvious that this volume change is essentially the algebraic sum of three separate volume-changes:

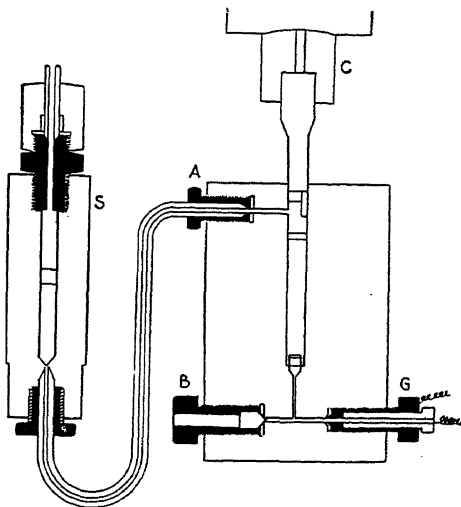


FIG. 85 (XII)

- (1) The compressibility of the given solid
- (2) The compressibility of the liquid
- (3) The distortion of the container or bomb

Thus, if (2) and (3) can be evaluated, we obtain the value of (1).

The direct determination of the values of (2) and (3) is not easy, so the method adopted was that of repeating the observations with a body of known compressibility. In effect, then, the measurement is one of the compressibility of the given body relative to a standard body. In the present instance the standard body selected was soft steel, the compressibility of which had already been determined by Bridgman by a direct method. To obtain reliable results the details of the method must be studied closely; for an account of these the original paper should be consulted. For the measurement of the pressure inside the bomb advantage was taken of the change of electrical resistance of a metallic wire when exposed to pressure. Manganin

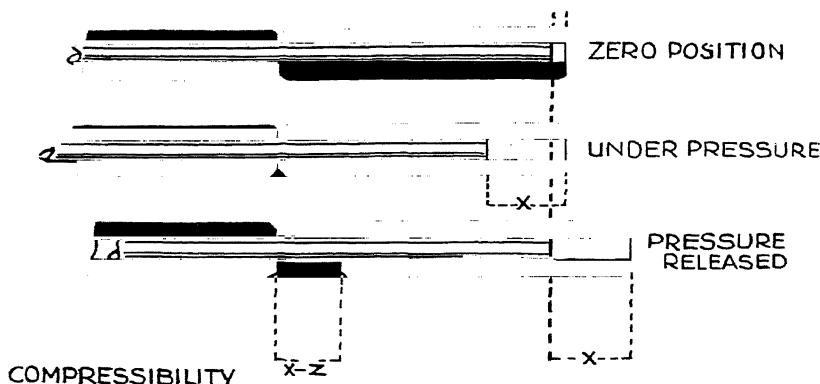


FIG. 86 (XII)

wire or similar alloy is suitable. The change of resistance was measured by a type of Wheatstone bridge.

The displacement of the piston was measured by means of Ames' dial micrometers.

In compressibility measurements the unit of pressure is the megabar. A megabar is equal to  $10^6$  dynes per square centimetre, and is 0.987 atm. In the present work pressures up to 12,500 megabars were used. This pressure was produced by means of a hydraulic press.

Determinations of the compressibilities of liquids have been carried out on somewhat the same lines.

An apparatus has been designed by Hyde<sup>1</sup> for the rapid estimation of compressibilities under high pressure. The apparatus consists of a small strong steel cylinder closed at one end and fitted with a plunger carrying a sleeve at the other (Fig. 86 (XII)). The cylinder is filled with the liquid under experiment, and it is arranged that the plunger stands inside the

<sup>1</sup> *Proc. Roy. Soc.*, 1920, 97, 252.

cylinder for about eight diameters at the commencement. The whole is immersed in a tube of the liquid and the pressure in this tube is raised to the desired value. The motion of the plunger necessary to equalize the pressure of the liquid inside and outside the small cylinder causes a movement of the sleeve relative to the plunger. The sleeve is provided with springs which cause it to remain in its new position on the plunger when the pressure is released and the latter moves to its original position relative to the cylinder.

Measurements are made of the position of the sleeve on the plunger, before and after the application of the pressure, and the decrease in volume of the liquid in the small cylinder thus determined. The bore of the cylinder was very accurately cylindrical and straight. Its mean diameter was measured to within 0.0005 cm., and the depth of the base to the face of the plug to within 0.002 cm. The capacity was checked by weighing the mercury content and by calculation from the dimensions. Measurements of the position of the plunger relative to the cylinder and sleeve were made by means of a depth micrometer. The whole was supported in an oil bath, the temperature of which was constant to 0.1°. The compressibility is determined from the ratio of the micrometer reading to the length of the liquid column.

The method used for the determination of compressibility consisted in the determination of the difference between the compressibility of each substance and that of mercury, which is assumed to be known. By adding to the difference so obtained the compressibility of mercury that of the substance is obtained.

The apparatus consists of a piezometer of glass which is first wholly filled with mercury and subjected quantitatively to pressure and then afterwards partly filled with the liquid in question (displacing an equal volume of mercury), and again subjected to quantitative compression. The diminution of volume was determined by allowing the mercury to make contact with a very finely pointed platinum wire, the changes in volume being measured by weighed globules of mercury. Thus the difference between the compressibility of the substance and that of mercury may be determined very simply from the difference between the two parallel series of compressions; and the compression of the apparatus is entirely eliminated from the result, occurring equally in the two series.

Various forms of piezometer, all depending upon the same principle, were used. The accompanying illustration shows two forms found suitable (Figs. 87 (XII) and 88 (XII)). It was filled with mercury and the change in volume for different pressures was measured very simply by placing the whole jacket in the pressure apparatus, adding successive weighed quantities of mercury and determining the pressures needed just to break and then again to make the electrical connexion between the meniscus and the platinum point. This electrical method gives very reliable results. The given liquid was then either directly introduced into the piezometer or enclosed in a thin glass cigar-shaped bulb and slipped in. The weight of the liquid was determined both by weighing it before its introduction to the piezometer and obtaining the change in weight of the piezometer after its introduction, due allowance being made for the displaced mercury which was removed. The series of measurements was then performed as previously. Small mercury pipettes with exceedingly fine long-drawn-out jets serve to

add and remove the small quantities of mercury. Densities were taken at 20° by means of the Ostwald-Sprengel pyknometer and from the weighings the corresponding volumes were obtained.



FIG. 87 (XII)

FIG. 88 (XII)

The piezometer was compressed in the steel barrel of the high-pressure pump manufactured by the Société G n voise. The barrel was half filled with mercury and the rest with pure castor-oil. The piezometer was suspended from the bronze cap provided with the instrument, by means of two stout brass hubs screwed into its lower surface. The barrel was immersed in a thermostat, as constant temperature is essential for accurate work. For the calculation, weighings are converted into volumes and the constant of compressibility, i.e. the decrease in unit volume for unit pressure increase, is computed. The compressibilities of substances at very high pressures have been investigated also by Bridgman. A description of a primary gauge for high pressures designed by him is given in this Chapter in Section 8 (Pressure).

**Tensile Strength of Liquids.** That powerful cohesive forces act between molecular layers in the interior of a liquid has long been recognized. Donny in 1846 found that it was

possible for a column of sulphuric acid 1.255 metres long to hang in a vertical glass tube sealed at the upper end, even when the atmospheric pressure was removed from the lower end. He explained this phenomenon as due to the adhesion of the sulphuric acid to the glass and to the cohesion of the liquid itself. Berthelot a few years later succeeded in showing that water has a very considerable cohesion, and under proper conditions can sustain a great tensile stress. His method consisted in completely filling a capillary tube with water at 28° or 30°, and sealing both ends. If the tube is then cooled to 18° the water does not contract, but still occupies the whole volume of the tube. The tensile strength of the water is thus resisting the natural contraction due to cooling.

Dixon measured the tensile strength of water according to the method of Berthelot. Eight capillary tubes were used, length varying from 22 to 15 cm., and all 1.0 mm. bore. The tubes were first cleaned, a piece of yew wood introduced, and after being filled with air-free water, were kept submerged in boiling water for 1 hour or so. Before sealing the drawn-out end the water was allowed to cool and a millimetre or more of the bore was cleared of water by warming the point in the flame. The fine end was then sealed. Observations were then made of the temperatures at which the tube was full and, after slow cooling, at which rupture took place. The tension may then roughly be determined from the formula

$$B = \frac{1}{\bar{V}_1} \cdot \frac{V_1 - V_2}{P_2 - P_1}$$

Where  $B$  = the coefficient of compressibility of water

$V_1$  = Volume under lower pressure  $P_1$

$V_2$  = Volume under increased pressure  $P_2$

A tension  $P_2$  will bring about the same change in volume in the opposite sense. The apparent change in volume of the water must be corrected for the contraction of the cooling glass. This may be allowed for by the formula

$$P = \frac{(\alpha - g)(t_2 - t_1)}{\beta[1 - \alpha(t_2 - t_1)]}$$

$P$  = tension

$\alpha$  = coefficient of expansion of water over the range

$g$  = coefficient of cubic expansion of glass =  $2.4 \times 10^{-5}$

$t_1$  = temperature of rupture

$t_2$  = temperature when tube is full

Introducing the correction for the elastic yield of the glass, we get

$$P = \frac{(\alpha - g)(t_2 - t_1)}{\beta[1 - \alpha(t_2 - t_1)]} + \frac{1}{R^2 - r^2} \left( \frac{r^2}{k} + \frac{R^2}{n} \right)$$

where  $R$  = external radius of tube

$r$  = internal radius of tube

$k$  = compression modulus of glass  $4 \times 10^5$  atm.

$n$  = tension modulus of glass  $3 \times 10^5$  atm.

The constants  $\alpha$  and  $\beta$  were obtained from the Landolt-Börnstein tables.

The values of  $P$  thus obtained had a least value of 37.7 atm. and a maximum value of 158.4 atm.

In making the observations the tubes were set in a large beaker of water. The temperature at which the tube became filled was first approximately determined and then, by slow heating in the correct neighbourhood, the exact determination was made. The large amount of water in the beaker ensures slow cooling, so that the temperature of reappearance of the bubble could be determined accurately.

Rosinger and Vettors<sup>1</sup> have determined the tensile strength of certain jellies by a method that depends on the static loading of jelly membranes. It is based on the fact that a circular elastic membrane supported rigidly at the circumference and subjected to air pressure on one side takes up a spherical form. The thickness of the film is measured with a microscope by attaching a scale to an adjusting screw and focusing on the top and bottom surface of the membrane. The height of the spherical segment is obtained from its volume. The original should be consulted for details of apparatus and the mathematical treatment of the method. The method is applicable to the study of any elastic medium that can be formed into a membrane.

<sup>1</sup> *J. Amer. Chem. Soc.*, 1927, 49, 2994.





# CHAPTER XIII

## MOLECULAR PROPERTIES

### SECTION 1: SOLUBILITY

**T**HE cases which will be dealt with in the present chapter are the solubilities of:

- I. Gases in liquids
- II. Liquids in liquids
- III. Solids in liquids

#### I. SOLUBILITY OF GASES IN LIQUIDS

Here we may distinguish two cases:

(a) The solubility of slightly soluble gases such as oxygen or carbon dioxide.

(b) The solubility of very soluble gases such as hydrochloric acid or ammonia.

**Method of Expression.** The solubility of a gas in a liquid may be expressed in various ways:

1. The volume of the gas measured at the temperature and pressure of the experiment, dissolved in a given volume or mass of the solvent.

2. The volume of the gas corrected down to what it would occupy at 0° and 760 mm. pressure dissolved in a given volume or mass of the solvent.

When the volume of the solvent is 1 ml., the solubility expressed in either of these ways is called the absorption coefficient.

3. With more soluble gases, the mass of the gas dissolved in a given volume or mass of either solvent or solution may be used.

4. The solubility may be calculated as gram molecules of solute to gram molecules of solvent.

In order that comparisons shall be possible between solubilities expressed in these different ways, it is very desirable that in addition to a clear statement of the definition of solubility used, determinations of the densities of the solutions should also be given. Omission of the last determination frequently makes impossible the comparison of results of different experiments.

**The Preparation of Gas-free Solvent.** The solvent to be used will first be purified by the ordinary processes and must then be freed from dissolved gases; as an example, we can take the preparation of air-free water. The dissolved air may be removed by boiling, by a reduction of pressure or a combination of both processes. A round-bottomed flask is

fitted with a rubber stopper with a short glass tube passing through it, to which is fitted a short length of pressure tubing with a screw-clip. The flask is filled two-thirds full of water (distilled) and is boiled freely for 15 minutes; while it still boils the clip is closed and at the same time the flask is removed from the source of heat, so as to avoid a rise of pressure inside sufficient to blow out the stopper. The flask and its contents can then be cooled under the tap. Or a distilling flask containing the distilled water can be closed with a rubber stopper and connected by means of rubber tubing and a clip to a good water pump. Nearly all the air will have been removed in half an hour and if necessary the removal can be accelerated

by warming the flask: in the latter case a reflux condenser can be fitted between the flask and the pump. The clip is of course closed before the pump is stopped.

#### Determination of the Solubility of Slightly Soluble Gases.

The apparatus as shown in Fig. 1 (XIII) consists of an absorption pipette A, a measuring tube B, and a levelling tube C, fitted by means of clips to a stand which conveniently has a scale between B and C to enable experiments to be made at pressures other than atmospheric; *a* is a single-way tap and *b* and *c* are three-way taps. A and B are sometimes connected with metal tubing and sometimes with thick-walled rubber tubing. The measuring vessel B is graduated in millilitres and is filled with mercury. The tap *a* is connected to the vessel containing the gas-free solvent, by means of the rubber tube, and is kept opened. The three-way tap *c* is connected to the pump and A is exhausted. By opening the clip and tilting the vessels, A may now

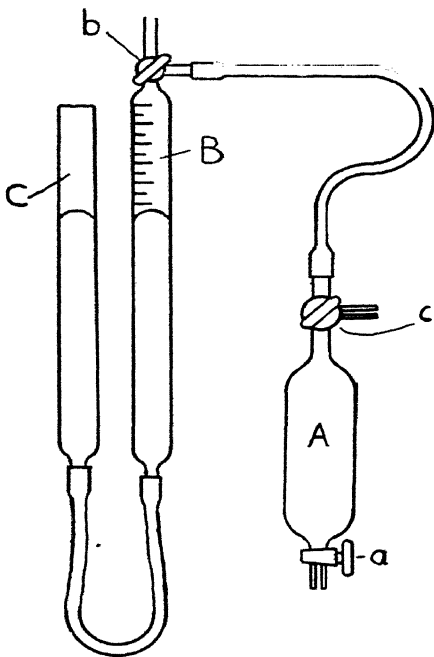


FIG. 1 (XIII)

be filled with gas-free solvent and the taps *a* and *c* are then closed. The capillary above B is next connected to the gas supply and *c* and *b* are opened so that the tube is filled with the gas; by closing first *b* and then *c* this will be at atmospheric pressure when the pump is off. Tap *b* is turned so that gas enters the measuring tube B, where it is saturated with water vapour by means of a drop of water previously introduced above the mercury. Tap *b* is closed and the mercury in B and C levelled. After standing for 10 minutes, the temperature, volume, and pressure of the gas in B are read. A and B are now connected, C is raised, and 20 ml. of solvent run out of *a* into a 20-ml. flask. The tap *a* is closed and the apparatus

gently shaken to hasten the absorption of the gas. C and B are levelled and the apparatus is again shaken. If the level in B is altered, C must be again adjusted and shaking repeated until it is found that no further absorption occurs. Again allow to stand for 10 minutes and read off the temperature, volume and pressure of the gas in B. If the temperature and pressure are the same for both the volume measurements, the volume of gas absorbed is  $V_1 - V_2 - 20$ . The volume of solute is now found by running it out into a measuring vessel. The volume of solute run out in the first instance (taken above as 20 ml.) can be determined more accurately by weighing (making allowance for what is left in the capillary below the tap *a*), and the same applies to the volume of the solution. The volume of gas absorbed is measured as a moist gas at temperature  $t$  and pressure  $p$  and can be corrected down to dry gas at  $0^\circ$  and 760 mm. In case the barometric pressure and the temperature have altered during the experiment, the volumes  $v_1$  and  $v_2$  will be corrected down to dry gas at  $0^\circ$  and 760 mm. before subtracting. The same apparatus can be used for measuring the solubility at different temperatures where A alone is placed in the thermostat, and for pressures other than atmospheric. In the general case

Let  $V$  = volume of solvent remaining in A

$x$  = volume of solvent run out of A

$y$  = volume of gas in B at the start, measured at temperature  $T^\circ \text{K}$ , pressure  $P$  mm. and aqueous vapour pressure  $f$

$z$  = volume of gas in B at the end, measured at temperature  $T_1^\circ \text{K}$ , pressure  $P_1$  mm. and aqueous vapour pressure  $f_1$

$T_2$  = the temperature of A on the absolute scale

$f_2$  = the vapour pressure of the solvent at  $T_2^\circ \text{K}$

Then the volume of dry gas at the start is :

$$\frac{y(P - f)273}{T \cdot 760}$$

The volume of dry gas in B at the end is :

$$\frac{z(P_1 - f_1)273}{T_1 \cdot 760}$$

The volume of dry gas in A at the end is :

$$\frac{x(P_1 - f_2)273}{T_2 \cdot 760}$$

Therefore the absorption coefficient at temperature  $T$  and pressure  $P$  is :

$$273 \left\{ \frac{y(P - f)}{T} - \frac{z(P_1 - f_1)}{T_1} - \frac{x(P_1 - f_2)}{T_2} \right\}$$

$$V \cdot 760$$

The dimensions of the apparatus must obviously be chosen with due regard to the solubility of the gas being measured. With a gas such as oxygen, a large absorber and a narrow measuring tube are necessary. In the case of a number of gases which are only slightly soluble, such as oxygen and carbon dioxide, suitable analytical methods are available for the determina-

tion of the amount of gas present in the solution and in such cases more accurate results are obtainable by this means than by the direct measurement of the volume of gas dissolved.

**Solubility of Oxygen in Water.** As an example we may take the determination of the solubility of oxygen in water. Measurements of this quantity have been made by Winkler and Whipple. The latter forced the gas through 3 litres of water and took samples from time to time; he found that several hours were sometimes required to reach saturation. A 3-litre bottle filled with distilled air-free water is placed in the thermostat, and purified oxygen is bubbled through. Samples are taken in a 250 ml. narrow-necked bottle fitted with a glass stopper. In taking the sample, the glass stopper is replaced by a rubber stopper with a delivery tube extending to the bottom of the bottle and an exit tube passing to the bottom of the stopper only: the sample is drawn into the bottle by suction and at least one bottle-full in excess is drawn through to avoid disturbance of the equilibrium due to the air in the bottle at the start. The glass stopper is then placed in the bottle and the sample is ready for the determination. The solutions required are:

(a) 48 grams of manganous sulphate dissolved in water and made up to 100 ml.

(b) hydrochloric acid solution, specific gravity 1.18

(c) 70 grams of potassium hydroxide and 15 grams of potassium iodide dissolved in water and made up to 100 ml.

(d) N/40 sodium thiosulphate solution standardized against N/40 potassium bichromate solution

(e) freshly prepared starch solution

The alkaline potassium iodide solution precipitates manganous hydroxide, and this on acidifying with hydrochloric acid liberates an equivalent quantity of iodine which is titrated with the standard thiosulphate.

The glass stopper is removed from the sample, and by means of a 1-ml. pipette this quantity of manganous sulphate is added. The pipette is lowered to the bottom of the bottle before the solution is allowed to run out; 1 ml. of the alkaline iodide solution is then added in the same manner and the glass stopper inserted (whereby 2 ml. of water are forced out and no air bubble is left in the bottle).

The bottle is then turned until the contents are thoroughly mixed and allowed to stand until the precipitate settles; 1 ml. of hydrochloric acid is now added in the way described above, the stopper is again replaced, whereby 1 ml. of the supernatant liquid is forced out, and the contents are well mixed; 200 ml. of the contents are now transferred to a flask and titrated with the N/40 thiosulphate, adding a few millilitres of the starch solution when the solution has become a faint yellow. The number of millilitres of thiosulphate used gives the solubility in milligrams per litre. In very accurate work the corrections for the 2 ml. of water forced out when the stopper is replaced after the addition of the manganous sulphate and the alkaline iodide solutions may be applied. Observations of the temperature and barometric pressure at which the solution was saturated are of course recorded.

When it is desired to determine the solubility of a gas at pressures less

than atmospheric this can conveniently be done by diluting the gas with another, e.g. if air be used in the above experiment at a total pressure of 760 mm., the oxygen, being 20.8 per cent of the mixture, is under a partial pressure of  $0.208 \times 760 = 158.1$  mm. and the solubility of the oxygen measured is that of oxygen under this pressure.

**Determination of the Solubility of very Soluble Gases.** All the very soluble gases are either acid in solution, such as sulphuretted hydrogen and sulphur dioxide, or alkaline, such as ammonia, so that suitable analytical methods are always available. Suppose the solubility of hydrochloric acid gas in water is to be measured. A thin-walled glass vessel of the shape shown in Fig 2 (XIII) is first cleaned, dried and weighed; it is then filled with water and weighed again to find its volume. About 15 ml. of distilled water are placed in the bulb so that it is half full and the apparatus is placed in the thermostat: a slow current of the gas is then passed through the arm *a* and is allowed to pass until the water is saturated, the arm *a* is then sealed off and finally the arm *b*. The tube is then carefully dried and weighed, thus giving the weight of the solution. File marks are made above and below the bulb, which is placed in a strong beaker containing 300 ml. of N sodium hydroxide solution and with the aid of a glass rod is broken to pieces while the bulb is well below the liquid. The excess of alkali is then titrated with normal hydrochloric acid. A sample of the saturated solution prepared in a similar way at the same time is used for a density determination; the weight of solution used in the solubility determination is known and its volume can now be calculated, and knowing the volume of the whole tube a correction can be applied to the solubility for the volume of the hydrochloric acid gas above the solution.

The absorption coefficient of a gas (*k*) is the volume of gas (in millilitres) calculated at N.T.P., absorbed by 1 ml. of the liquid at a given temperature when the partial pressure of the gas is 760 mm. The following table gives the solubility of a number of gases in water at 20°

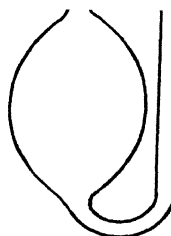


FIG. 2 (XIII)

Gas	<i>K</i>
Hydrogen	0.0184
Helium	0.0138
Nitrogen	0.016
Oxygen	0.0314
Argon	0.037
Carbon monoxide	0.0232
Carbon dioxide	0.878
Methane .	0.0331
Ethane .	0.0472
Ethylene .	0.122
Ammonia .	715.4
Nitrous oxide	0.63
Nitric oxide	0.047
Hydrogen sulphide	2.67

## II. SOLUTIONS OF LIQUIDS IN LIQUIDS

When two liquids are shaken together they may be (a) miscible in all proportions, (b) immiscible, (c) partially miscible. The latter case alone concerns us. In this case we may get one phase or two present, depending on the proportions of the two substances in the mixture. When two phases are present, the one having the lower density will float on the top of the other and each phase will be a saturated solution, one of A in B and the other of B in A. When a single phase is present it will in general be an unsaturated solution. Two methods are in use for determining the solubilities, 'the analytical method' and the 'synthetic method'.

**Solubility of Phenol in Water.** As an illustration we may take the determination of the solubility of phenol in water.

*Analytical Method.* In the analytical method, 250-ml. bottles with glass stoppers are used; 60 grams of phenol and 120 grams of water are placed in the bottle, the stopper put in position and, if desired, a rubber cap can be tied over the stopper and neck of the bottle. The bottles are placed in the thermostat and shaken for 2 hours. The shaking is stopped, the bottles are placed in a vertical position with the stoppers only projecting and allowed to stand until the two layers have separated out. 10 ml. of the upper layer are removed by means of a pipette, transferred to a stoppered conical flask and weighed, and the amount of phenol present is determined by the use of a standard bromine solution by the method of Koppeschaar. The bottle is then closed and shaken for another hour, after which another 10 ml. of the top layer is taken for analysis. This process is continued until two successive analyses agree, showing that the top layer, and by inference the bottom layer, are both saturated. 10 ml. of the bottom layer are now removed and analysed in a similar way; the finger is placed over the top end of the pipette and the lower end is introduced into the lower layer; the finger is then removed and the liquid drawn up. After removing the pipette, the outside is carefully dried to remove any adhering portions of the upper layer which might drain down, and the liquid examined to see that none of the upper layer is present; if this is found to be satisfactory the solution can be weighed and analysed. Further experiments are conducted in the same manner at other temperatures. The method of analysis used will of course depend on the nature of the two liquids and must be chosen to meet each individual case. In some cases physical methods may be found to be the most suitable, or it may happen, when their boiling-points are widely different, that one liquid can be evaporated off from the other. Again the amounts of the substances to be added in the first instance must be determined by experiment; equal quantities generally will be tried first and it may then be found that one liquid goes completely into solution in the other or that there is only a small quantity of one layer—in this case more of the deficient substance must be added and shaking resumed until the amounts of each of the two layers are sufficient for examination.

*Synthetic Method.* In the synthetic method a number of soft glass tubes are prepared and the phenol and water are weighed out into these in a series of approximate ratios 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1, and

the tubes are then sealed up. One of the tubes is now taken and heated with shaking until the contents become homogeneous; it is then placed in a large bath of water at this temperature and the bath is allowed to cool slowly. Suddenly an opalescence will appear in the tube, and the temperature of the bath is noted: the opalescence is due to the appearance of the two phases, solution of B in A and of A in B. It is possible to get the temperature at which the opalescence appears on cooling much more exactly than that at which the two phases disappear on heating. The temperature and the composition of the mixture are now plotted as one point on the solubility curve. When all the values have been plotted the gaps in the curve will be apparent and the mixtures having approximately the composition required can be made up and the solution temperatures may be determined.

### III. SOLUTIONS OF SOLIDS IN LIQUIDS

A discussion on the solubility of solids is given by Hulett and Allen.<sup>1</sup> They point out that the solubility of small particles is greater than that of a plane surface. In the case of gypsum it was found possible to prepare solutions containing 20 per cent more solute than a normal saturated solution, i.e. one in equilibrium with a plane surface, by shaking with particles having a diameter of 0.3 micron. Even plates of gypsum when vigorously stirred with water gave a solubility 5 per cent too high owing to the ease with which the crystals break up to fine powder, and normal results were only obtainable by rotating the water over the gypsum plates by means of a stirrer working at 50 revolutions per minute. Using a fine powder and gentle stirring a high solubility was first obtained and then as the fine particles went into solution and the larger ones increased in size the solubility dropped to the normal value, but the process is a slow one and equilibrium was not reached for five days. They also point out the necessity for density determinations, since results are variously expressed as:

- (a) Grams of solute in 100 grams of solvent
- (b) Grams of solute in 100 grams of solution
- (c) Grams of solute in 100 ml. of solution
- (d) Gram molecules of solute in 100 gram molecules of solvent

In order to make certain that equilibrium has been reached it is best to approach it from both sides—in one case by stirring the solid with the solvent and in the other by stirring a supersaturated solution with the solid. Since in most cases the solubility of a solid increases with rise of temperature the supersaturated solution is prepared by heating the powdered solid with water at a higher temperature than that of the determination for a short time, say 20 minutes.

*Method of Agitating Solutions.* The necessary agitation can be secured by means of the arrangement described by Noyes, shown in Fig. 3 (XIII), where the bottles act as stirrers in the thermostat. The bottles are of about 500 ml. capacity and are steamed out before use. The solid, consisting of some large particles and a quantity of fine powder (which goes into solution more quickly owing to its larger surface area), is placed in two of the bottles

<sup>1</sup> *J. Amer. Chem. Soc.*, 1902, 24, 667.



together with the distilled water or other solvent to fill them three-quarters full. In the other two bottles a few large particles of the solid and supersaturated solution are placed. The flat-topped glass stoppers are inserted and if desired a small rubber cap is tied over them. The bases of the bottles fit into recesses in the central wooden disc *a* and the end discs *b* are then rotated along the screw until they press against the stoppers and hold the bottles in position. The discs *b* are fixed by means of the metal nuts shown. Another method consists in fixing a conical flask or a large tube 25 by 2.5 cm. in a vertical position, closing the neck with a rubber stopper through which passes a glass tube extended to a flat piece at the top which acts as a guide and bearing for the rod of a glass stirrer.

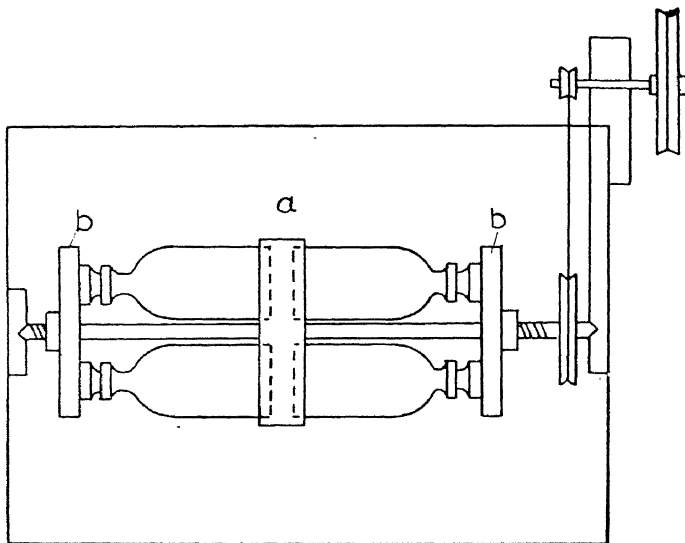


FIG. 3 (XIII)

Soluble substances generally go into solution more readily than slightly soluble ones, and in general 4 hours' stirring will be sufficient for equilibrium to be set up: with less soluble substances this time may be extended to days.

*Method of Procedure.* After 4 hours the stirrer is stopped and the bottles removed and hung in the thermostat with their necks projecting from the water; when the solid has subsided the clear solution is ready for removal. When the tube form of apparatus is used, a second hole is sometimes bored in the rubber stopper and a short piece of glass tube fitted in it through which the pipette can be inserted for the removal of the solution; this tube is stoppered during the stirring. Various forms of apparatus have been devised for the removal of the solutions; in all cases the latter is filtered to avoid the introduction of minute particles of suspended solid. Lowry used the tube shown in Fig. 4 (XIII), the end of which is covered with two thick sheets of filter paper and a layer of linen held in place by a rubber band. The tube

is warmed to the temperature of the bath and lowered into the solution, which filters in; the tube is then quickly removed and its contents poured into the weighing vessel. Again a small 25-ml. Sprengel pyknometer with glass caps can be used. The pyknometer is weighed and its end fitted with a piece of rubber tube holding a piece of glass tubing plugged with cotton-wool. The solution is drawn up to the mark with the pyknometer in the thermostat, the caps put on and the density determined. The contents of the tube are then washed out with solvent. Another pipette for the same purpose is shown in Fig 5 (XIII). The stopcock *f* is attached to the graduated end of the pipette with rubber tubing, and the filter tube *e*, containing cotton-wool, is attached to the lower end. With both taps open the solution is drawn up until it reaches the graduated part of the tube: the upper tap is then closed, the pipette removed from the solution, the lower tap closed, the connexions *e* and *f* removed, and a rubber cap placed over the open end *b*. Any solution in the capillary below the tube is removed by means of a filter paper and the pipette and its contents are weighed. If the pipette has been previously calibrated with water, the density can be determined and the contents can be washed out completely with solvent.

**Evaporation of Solutions.** When the dissolved substance is stable the weight of it present in a known weight of solution is found by evaporation. Great care must be used to avoid loss by spattering; with aqueous solutions evaporation on the water bath is used, covering the dish with a large condensing funnel to prevent dust falling in. Deep evaporating basins with flat bases and made of thin glass with glass covers are convenient. After evaporating to dryness the dishes are heated to constant weight in the air oven at 110°. If the densities and solubilities for all four samples agree, it may be taken that equilibrium had been reached and the solubilities are correct. In case of disagreement a further period of stirring must be used. A form of apparatus specially devised for the purpose is the Liebig drying tube shown in Fig. 6 (XIII). As shown, this has a loosely fitting draught tube *c* between which and the drying tube a strip of filter paper is placed to prevent solvent condensed in *c* running back on to the solid. This form was also used in Ostwald's laboratory by Trevor. The form of the tube is intended to avoid loss by spurting. T. W. Richards evaporated his solutions in small quartz flasks in an electric oven at 103°. The flasks had long necks and a tube passed down the neck to 4 cm. above the surface of

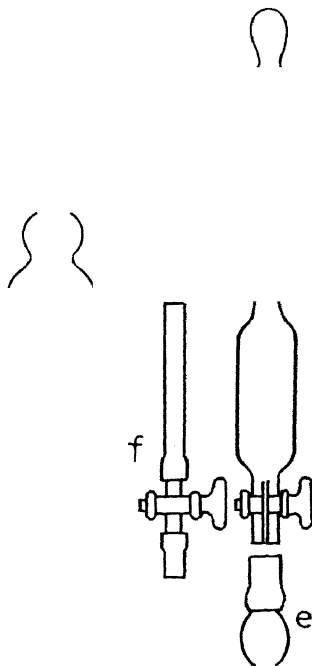


FIG. 4 (XIII)

FIG. 5 (XIII)

the solution ; dry air was passed down the tube and the tube and flask were weighed together. Substances which are not stable to heat may be determined in some cases by chemical analysis and in others by making use of

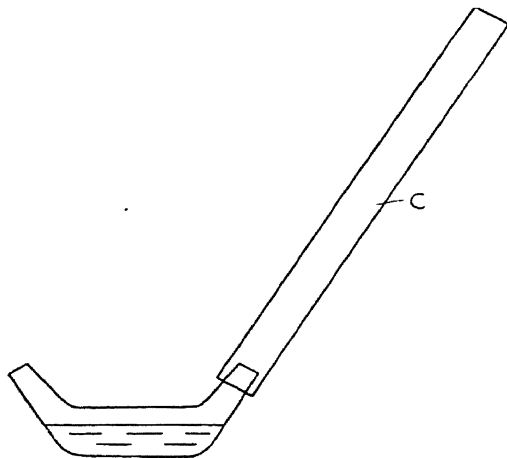


FIG. 6 (XIII)

some physical property. The latter is often very convenient when a large number of determinations have to be made. If a dipping refractometer is available, this may be most useful ; or the electric conductivity can be used, or the density of the solutions. In either case the first step is to make up a series of solutions of known strength and measure the physical property in question for these solutions. Then, when the composition of an unknown solution has to be determined, the property in question is measured for this solution or for a given weight of this solution diluted with

a known weight of solvent ; referring to a large-scale curve the composition of the diluted solution can be obtained and from this, that of the undiluted one calculated.

**Flotation Equilibrium.** In this connexion the method of floating equilibrium is very convenient. Floats of the capacity of 5 ml. and the shape shown in Fig. 7 (XIII) are used ; these are made of glass and weighted with mercury, the weight being finally adjusted by sealing bits of glass on one end. They float or sink with a density change of  $2 \times 10^{-7}$  corresponding to 0.002 per cent of sodium chloride. Small beads of known specific gravity can also be purchased from makers of hydrometers and used when less accuracy is desired. Solutions are prepared in which the float sinks and solvent is added until the float just rises. The temperature is recorded and the solution analysed. A beaker and the float are weighed, the solution to be determined is added and the weighing repeated, solvent is then added with stirring (the temperature of the original determination being maintained) until the float rises. The beaker and its contents are weighed again. The degree of dilution is thus known and the diluted solution has the same composition as the original solution.



FIG. 7 (XIII)

In the case of very slightly soluble salts such as silver chloride, the methods described above are unsuitable. In such cases the electrical conductivity of the solution can be used to measure the concentration. The requirements of the method are that the saturated solution shall be so dilute that the equivalent conductivity may be taken to be the same as

the conductivity at infinite dilution, and yet this equivalent conductivity must be much greater than the specific conductivity of water. For example, a solution of silver chloride saturated at 18° had a specific conductivity  $2.4 \times 10^{-6}$  reciprocal ohms, that of water at the same temperature being  $1.16 \times 10^{-6}$  ohms.

Given that

$$\begin{aligned}\lambda_{\infty} \text{KCl} &= 131.2 \\ \lambda_{\infty} \text{AgNO}_3 &= 116.5 \\ \lambda_{\infty} \text{KNO}_3 &= 126.1 \\ \lambda_{\infty} \text{AgCl} &= \lambda_{\infty} \text{AgNO}_3 + \lambda_{\infty} \text{KCl} - \lambda_{\infty} \text{KNO}_3 \\ &= 116.5 + 131.2 - 126.1 \\ &= 121.6\end{aligned}$$

Now K due to  $\text{AgCl} + \text{H}_2\text{O} = 2.4 \times 10^{-6}$  ohms $^{-1}$  per ml.

K due to  $\text{H}_2\text{O} = 1.16 \times 10^{-6}$  ohms $^{-1}$  per ml.

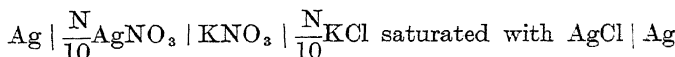
$\therefore$  K due to  $\text{AgCl} = 1.24 \times 10^{-6}$  ohms $^{-1}$  per ml.

Or for 1,000 ml. with electrodes 1 cm. apart  $1.24 \times 10^{-3}$  ohms

$\therefore$  Number of molecules per litre of  $\text{AgCl}$

$$\frac{1.24 \times 10^{-3}}{121.6} = 1.02 \times 10^{-5}$$

Another method consists in measuring the E.M.F. of a cell, e.g.



The E.M.F. at 25° was 0.45 volts, the fraction of  $\text{AgNO}_3$  dissociated in N/10 solution is found from the conductivity to be 0.82.

$$\text{Now } E = \frac{0.0002T}{n_c} \log \frac{c_1}{c_2}$$

$$\log \frac{c_1}{c_2} = \frac{0.45}{0.0002 \times 298} = 7.55$$

$$\therefore \frac{c_1}{c_2} = 3.548 \times 10^7$$

$$c_1 = 0.82 \times \frac{1}{10} \text{ gram molecules per litre}$$

$$c_2 = \frac{0.082}{3.548} \times 10^7 \text{ gram molecules per litre}$$

$$= 2.31 \times 10^{-9} = C_{\text{Ag}}$$

Now N/10 KCl is 0.85 per cent dissociated.

$$\therefore C_{\text{Cl}} = 0.085 \text{ molecules per litre.}$$

$$\begin{aligned}\therefore C_{\text{Ag}} \times C_{\text{Cl}} &= 2.31 \times 10^{-9} \times 0.085 \\ &= 1.96 \times 10^{-10}\end{aligned}$$

In solutions containing silver chloride only

$$C_{\text{Ag}} = C_{\text{Cl}} = C_{\text{AgCl}} = \sqrt{1.96 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ molecules per litre}$$

## SECTION 2: MOLECULAR WEIGHTS

**Introduction.** Van't Hoff showed that substances in dilute solution are in a state similar to that of a gas, and that if the osmotic pressure of a solution of known concentration can be determined at a known temperature, it is possible to calculate the molecular weight (see below).

If the solute be associated or dissociated in solution, abnormal values for the molecular weight are obtained.

The osmotic pressure of a solution is related to the effect of the solute in lowering the vapour pressure of the solvent, raising the boiling-point, lowering the freezing-point, lowering the transition temperature, and decreasing the solubility of the solvent in another solute. These can therefore all be used to find the molecular weight of the dissolved substance.

**1. The Osmotic-pressure Method.** The first accurate determinations of the osmotic pressure of solutions were carried out by Pfeffer, who found that a membrane of copper ferrocyanide precipitated in the walls of a porous earthenware pot could withstand the considerable pressures generated in the necessary experiments. Previously Traube had observed that such membranes were permeable to water or other liquids, but not to many dissolved substances. Such membranes are known as semi-permeable membranes and must always be employed in all determinations of osmotic pressure.

*Preparation of Semi-Permeable Membranes.* The air is removed from the walls of a porous cell by boiling it in water under reduced pressure and the cell is placed in a 3 per cent solution of copper sulphate until the walls are thoroughly impregnated with the salt. It is then washed with distilled water, filled with a 3 per cent solution of potassium ferrocyanide, and re-immersed in the solution of copper sulphate. A precipitate of copper ferrocyanide is formed in the pores of the cell near the inner surface. The cell is then thoroughly washed.

*Adie's Modification of Pfeffer's Method* (Fig. 8 (XIII)). The porous cell *a* is fitted with a glass tube *b*, the jointing being effected by means of sealing-wax; the tube is shown before connecting to a manometer, which contains mercury from

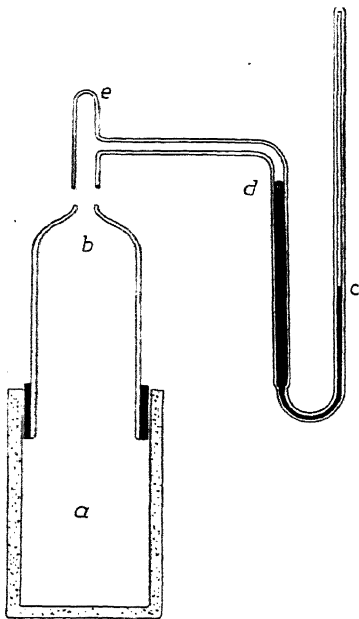


FIG. 8 (XIII)

*d* to *c* and air above this. A solution the osmotic pressure of which is being determined is poured into the cell through *e* until the remainder

of the apparatus is completely filled.  $e$  is sealed and the cell is then immersed in pure water. The whole apparatus is immersed in a thermostat. The water enters slowly and the pressure increases to a constant value after days or weeks. The amount of water which enters is so small that the dilution is not important, but where necessary it may be estimated by the diminution in the volume of the air.

That the final pressure so obtained is equivalent to the osmotic pressure, that is to the excess of pressure on the solution side of the membrane, can be deduced from theoretical considerations.

*Laws of Osmotic Pressure.* Quantitative experiments with dilute cane-sugar solutions of varying solution concentrations and at different temperatures show that for dilute solutions the osmotic pressure is directly proportionate to the concentration and approximately to the absolute temperature. The laws of osmotic pressure are, as pointed out by van't Hoff, similar to those relating to gaseous pressure. In other words, the osmotic pressure of a substance in dilute solution is equal to the pressure which it would exert as a gas at the same temperature and occupying the same volume as the solution if it could exist as a gas under such conditions. This is especially true of dilute (about 1 per cent) solutions.

*Calculation of Molecular Weight.* Hence, if  $P$  is the osmotic pressure of a solution at absolute temperature  $T$ , which contains 1 gram molecule of dissolved substance in volume  $V$ , then  $PV = RT$ , where  $R$  is the absolute constant corresponding to 1 gram molecule of any perfect gas. It is probably more correct to take  $V$  as the volume of the solvent rather than that of the solution.

If  $m$  grams of a substance of molecular weight  $M$  be dissolved in  $n$  grams of a solvent, and if the resulting solution has a density  $d$  at  $T^\circ$  absolute, the volume of solution =  $\frac{m+n}{d}$  ml.

If the osmotic pressure of the solution is  $P$  mm. of mercury at  $T^\circ$  absolute, then the osmotic pressure at  $0^\circ$  is =  $\frac{273P}{T}$  mm. And the osmotic pressure, if the volume of the solution is .41 litres,

$$\frac{273P}{T} \cdot \frac{m+n}{d} \text{ mm.} = \frac{273P}{T} \cdot \frac{V}{22,410} \text{ mm.}$$

if  $V$  is the volume of the solution in ml. at  $T^\circ$  absolute. Hence, since  $m$  grams exerts this pressure in 22.41 litres at  $0^\circ$ ,

$$760 \frac{22,410 \cdot T \cdot d \cdot m}{273P(m+n)} \text{ grams}$$

would exert a pressure of 760 mm. in 22.41 litres at  $0^\circ$  F.

$$\begin{aligned} \therefore M &= \frac{760 \times 22,410 \times T \times d \times m}{273 \times P \times (m+n)} \\ &= \frac{62,390 \times T \times d \times m}{P \times (m+n)} \\ &= \frac{62,390 \times T \times m}{P \times V} \end{aligned}$$

If  $P$  is expressed in atmospheres

$$M = \frac{82.09 \times T \times d \times m}{P \times (m + n)} \quad \frac{82.09 \times T \times m}{P \times V}$$

Conversely, the osmotic pressure of dilute solutions can be calculated approximately if the molecular weight of the solute in the solution be known.

*Anomalous Results.* If the solute under observation dissociates in solution into ions, abnormal values for the osmotic pressure are obtained. It appears that each ion produces its own specific effect as if it were a complete molecule. Conversely, if the substance is associated in solution, values lower than those expected are obtained for the osmotic pressure. Similar effects are observed in connexion with the lowering of solvent vapour pressure and the other phenomena related to osmotic pressure.

Owing to the difficulty of obtaining accurate results, and to the length of time required for the maximum osmotic pressure to be attained, osmotic-pressure determinations are very seldom employed to measure molecular weights.

*Example.* Pfeffer found that the osmotic pressure of a 1 per cent aqueous solution of cane-sugar is 493 mm. at  $0^\circ$ .

Here  $d = 0.996$ ,  $n = 100$ ,  $m = 1$ ,  $T = 273$ ,  $P = 493$

$$M = \frac{62,390 \times 273 \times 0.996 \times 1}{493 \times 10} = 341$$

Van't Hoff for a 1 per cent solution takes 1 gram of sugar and 100 grams of water and obtains a volume of 100.6 ml.

*Other Semi-permeable Membranes.* Other substances which may be employed as semi-permeable membranes include ferric hydroxide, gelatine tannate, calcium phosphate, Prussian blue and silicic acid. A large number of such membranes also occur naturally in plant and animal cells.

*Isotonic Solutions.* Solutions having the same osmotic pressure as each other are termed *isosmotic* or *isotonic*. Tammann describes an optical method of determining whether solutions are isotonic or not. A drop of potassium ferrocyanide at the end of a capillary pipette is immersed in copper sulphate solution, when a membrane of copper ferrocyanide is at once formed. According as the osmotic pressure inside is greater or less than outside, water enters or escapes and the cell expands or contracts. At the same time striae can be observed in the copper sulphate solution around the membrane owing to the changes in concentration produced. If water enters the cell an increase in concentration occurs and the striae descend. If water leaves the cell, a decrease takes place and they rise; with isotonic solutions none are visible. Other substances may be dissolved in either or both solutions before the cell is formed, and a variety of determinations carried out in this way.

*Osmotic Pressures of Concentrated Solutions.* Berkeley and Hartley have examined the osmotic pressures of concentrated solutions, using membranes of copper ferrocyanide capable of withstanding pressures exceeding 100 atm. Equations of the van der Waal's type were found to give a good representation of the results with cane-sugar solutions containing 850–180 grams per litre, but since the values of the critical point derived from such equations

are impossible, they can only be regarded as applicable in special cases. The calculation is generally not justifiable, since the value of the constant in van der Waal's equation is known to vary with the temperature.

Fig. 9 (XIII) shows the apparatus devised by Frazer and Myrick.<sup>1</sup> It consists of a porous clay cup with a membrane of copper ferrocyanide (K) deposited on its exterior. The solvent and not the solute can pass through this membrane. J is a bronze cylinder into which the cell is fastened by means of the plug P. R is a glass U-tube, held in the mouth of the cell by means of the rubber stopper Q. I is a solution to be measured. A is a piece of capillary tubing to which the manometer is sealed. In this apparatus pressures as high as 270 atm. can be measured. An equilibrium is reached in a few hours so that measurements are completed in a day.

In the Lotz and Frazer modification<sup>2</sup> an improved manometer is employed. This consists of a water interferometer. This osmotic apparatus is claimed to be quicker in action and more dependable. High pressure can also be measured.

*Osmometers for Solutes of High Molecular Weight.* Carter and Record<sup>3</sup> describe an osmometer working on the counter-pressure principle of Berkely and Hartley, in which the osmotic pressure is applied externally. A flat 'Viscacelle' membrane is compressed between the two ground ends of the two glass bulbs of the apparatus and is supported on a slightly convex perforated brass upper plate to prevent movement under changing pressures.

Dry 'Viscacelle' or 'Cellophane' (the non-moisture proof variety) swells up in water to a definite maximum and then becomes permeable to water and ordinary solutions. Alcohol exerts little or no swelling effect. Consequently any degree of swelling between these limits may be obtained by immersing the dried membrane in the appropriate alcohol-water mixture. After swelling the membrane is transferred to absolute alcohol and then may be used with any miscible organic liquid without altering the swelling or permeability.

**2. The Lowering of the Vapour Pressure.** If  $p_0$  is the vapour pressure of the pure solvent and  $p$  is that of the solution, then

$$\log (p_0/p) = \frac{P \cdot m}{RT_0}$$

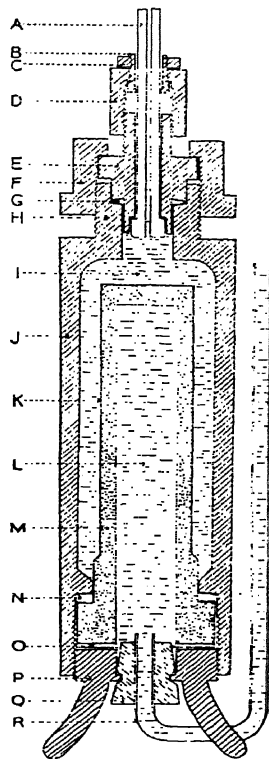


FIG. 9 (XIII)

<sup>1</sup> *J. Amer. Chem. Soc.*, 1916, 38, 1907. Cf. also Frazer and Lotz, *J. Amer. Chem. Soc.*, 1921, 43, 2501.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1921, 43, 2506.

<sup>3</sup> *J. Chem. Soc.*, 1939, 155, 660.



where  $P$  is the osmotic pressure,  $m$  the molecular weight of the solvent in the gaseous state, and  $\rho$  is the density of the solvent. Now

$$P = \frac{RT \cdot x}{V \cdot M}$$

where  $x$  is the mass of the solute of molecular weight  $M$  dissolved in  $V$  litres of the solution; therefore

$$M = \frac{xm}{\rho V} \bigg/ \log \frac{p_0}{p}$$

and when the difference between  $p_0$  and  $p$  is small this can be written

$$M = \frac{xm}{\rho V} \bigg/ \frac{p_0 - p}{p}$$

*Raoult's Method.* The earliest measurements on the relative lowering of the vapour pressure were made by Raoult, using a barometer tube (Chapter XII, S. 8). A small quantity of the solvent was first introduced into the Torricellian vacuum and the vapour pressure of the solvent thus measured; the vapour pressure of the solution was next determined in a similar manner. In this method it is difficult to ensure that the liquids are free from dissolved gases or other volatile substances and to overcome the variation in the superficial concentration of the solution due to evaporation and condensation; furthermore, the concentration of the solution, which is finally in equilibrium with the vapour in the space above the mercury, is not exactly known. The method is no longer used.

*Ostwald's Method.* An improved method was suggested by Ostwald and carried out by Will and Bredig; it consists in bubbling dry air first through the solution and then through the pure solvent. The air will take up from the solution a quantity of vapour proportional to the vapour pressure thereof and then from the solvent a further amount proportional to the difference of vapour pressure between the solution and the solvent; if the losses of weight  $w$  and  $w_1$  of the solution and solvent be determined, we have

$$\frac{w_1}{w} = \frac{p_0 - p}{p}$$

and from this the molecular weight of the dissolved substance can be determined.

The solution is placed in three Liebig's potash bulbs, A, B, and C, and the solvent in three more, D, E, and F. Each bulb is weighed and the six are connected together with tubing securely wired on. The six bulbs are wired to a piece of wood and fixed in the thermostat and dry air is aspirated through at the rate of about two or three bubbles per second for 2 hours. The air is dried by passing over soda lime: this can conveniently be contained in two straight tubes 1 inch in diameter and 3 feet long, placed side by side on a piece of board and connected together at one end by a piece of glass tube. This gives the same result as a very large U-tube, and it can be put at the back of the bench, where it will not occupy much space. After the air current is stopped the bulbs are removed, dried and weighed. Bulbs C and F should show practically no loss, thus indicating that the air was saturated with vapour with respect to their contents: if C shows no loss this means that the vapour pressure of the solution determined is that of a

solution having the original composition. The solution in A loses vapour and so alters in composition and has a lower vapour pressure at the end of the experiment than has C, the composition of which has not altered.

*Perman's Method.* Perman describes a method for determining the molecular weight by the lowering of the vapour pressure in which the apparatus shown in diagram (Fig. 10 (XIII)) is used. In this the inner tube B is exhausted by the water pump; mercury sufficient to act as a gauge is let in and allowed to run into B. The apparatus is again exhausted and weighed. The solution is made up by weight and is introduced by inverting the exhausted apparatus and opening the tap with the end of the tube in the solution. The solute is all washed in with small amounts of the solvent. The tube is then left open and the solution boiled down to half its bulk by heating B. The stopcock is turned, any liquid in the capillary above D removed, and the apparatus weighed to get the weight of the solution. The tube is now heated in the vapour jacket E. After 2 or 3 minutes the tap D is opened and readings are taken from 5 to 10 minutes after B begins to be heated by the vapour. Readings of the heights of the two mercury columns and of the liquid above them are taken. The tip C is then broken and these heights read again to

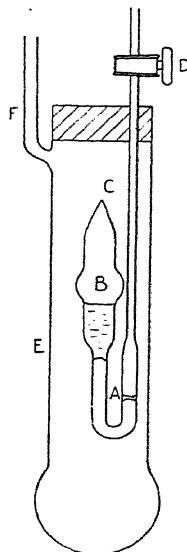


FIG. 10 (XIII)

get the relation between the density of the solution and that of the mercury; then

$$m = \frac{w.M.p.}{W.d}$$

where  $m$  is the molecular weight of the solute

$M$  is the molecular weight of the solvent

$w$  is the weight of the solute

$W$  is the weight of the solvent

$p$  is the barometric height, and

$d$  is the lowering of the vapour pressure

Good results were obtained with ether, chloroform and water as solvents.

*Wright's Method.* Wright<sup>1</sup> uses the apparatus shown in Fig. 11 (XIII). A weighed quantity of solute is placed in B; A and B are

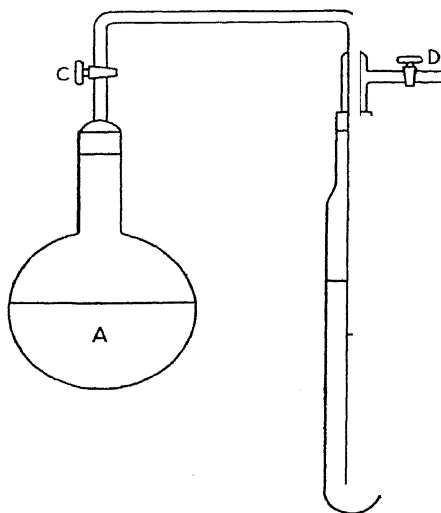


FIG. 11 (XIII)

half filled with solvent and the apparatus is connected to the filter pump to

<sup>1</sup> *J. Chem. Soc.*, 1919, 115, 1165.

boil out dissolved gases: after half an hour both taps are closed and the apparatus is allowed to stand for 2 or 3 hours. The tap C is then opened and the difference in height in B is measured. Capillarity is allowed for by opening the ground-joint of the flask A, after which B is removed and weighed to obtain the weight of the solution and so its composition. The molecular weight is then calculated by the ordinary formula, using a value for the vapour pressure of the pure solvent obtained from the tables. In the examples cited in the original paper the average error is about 6 per cent.

*Guglielme's and Blackman's Methods.* Guglielme<sup>1</sup> describes methods in which the vapour pressures are measured by methods similar to those used in hygrometry; for example, dew-point methods. Blackman uses two graduated test-tubes connected by an inverted T-piece, the arms of which are bent down to form an inverted U, with a bulb in each of the limbs of the  $\Omega$ . The unknown molecular weight is obtained by comparison with a substance of known molecular weight. The method consists in weighing out 0.05 to 0.1 grams of the substance into one tube and a similar amount of a substance of known molecular weight into the other. The tubes are then half filled with pure solvent, the T-piece connected and the tubes placed in a bath and heated to about 2° or 3° above the boiling-points of the solutions. Readings of the volumes are taken from time to time, and when the solutions have become isotonic the relation

$$\frac{m_1}{m_2} = \frac{V_2}{V_1}$$

will hold, where  $m$  is the molecular weight and  $V$  the volume. The best results are obtained by heating the bath to the temperature at which the more volatile solution boils; this solution will slowly diminish in volume while the other solution remains unchanged until equilibrium has been attained, when both will boil together. An accuracy of 3 per cent is attainable.

*The Methods of Barger and Rast.* Barger also uses a method which depends on the comparison of the vapour pressure of a solution of the substance of unknown molecular weight with that of one of a substance of known molecular weight. These methods are considered in more detail in the next chapter.

*Molecular Weight of Very Large Molecules.* For the determination of the molecular weight of substance of the nature of proteins, &c., the ultra-centrifuge of Svedberg, Carpenter and Carpenter<sup>2</sup> may be employed. For details of the determination of the molecular weight of casein, see original paper. With this method molecular weights of the order of 50,000 to 400,000 may be determined (see Chapter IV\*, S. 2).

**3. Boiling-point Methods.** This method is mainly due to the work of Beckmann. If the vapour pressure of a solvent is lowered by the solution therein of a non-volatile solute, it follows that the boiling-point at atmospheric pressure must be raised a proportional amount. If  $w$  grams of a

<sup>1</sup> *Atti R. Acad. Lincei*, 1901 (5), 10, 232.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1930, 52, 241, 270.

solute of molecular weight  $M$  be dissolved in  $W$  grams of solvent and the boiling-point is thereby raised  $\Delta T$ , then

$$m = \frac{K100 \cdot w}{W \cdot \Delta T}$$

where  $K$  is a constant, the molecular elevation of the boiling-point.  $K$  represents the rise in the boiling-point produced by dissolving 1 gram molecule of the solute in 100 grams of the solvent.

*Value of  $K$ .* The value of  $K$  can be found by experiment with substances of known molecular weight, and can be calculated from the relation

$$K = \frac{0.02T^2}{l}$$

where  $T$  is the absolute boiling-point of the solvent and  $l$  is the latent heat of vaporization per gram of the solvent.

Values of  $K$  for some of the more frequently used solvents are:

Solvent	Boiling-point	Ebulli-scope Const. <sup>1</sup>	Reference
Water . . .	100°	5.2	Beckmann, <i>Zs. Ph. Ch.</i> , 1891, 8, 223
Ammonia . .	— 33.46°	3.4	Franklin and Kraus, <i>Amer. Chem. Jour.</i> , 1899, 21, 13
Carbon disulphide	46.3°	23.7°	Menzies and Wright, <i>J. Amer. Chem. Soc.</i> , 1921, 43, 2320
Chloroform . . .	61.2°	36.6	Beckmann, <i>Zs. Ph. Ch.</i> , 1890, 6, 437
Acetone . . .	56.3°	16.7	
Ether . . .	35°	21.1	
Ethyl alcohol . .	78°	11.5	
Benzene . . .	80.3°	26.7	
Ethyl chloride	12.5°	19.5	Beckmann, <i>Zs. anörg. Ch.</i> , 1907, 55, 371
Ethyl bromide	37.7°	25.3	Beckmann, Fuchs and Gernhardt, <i>Zs. Ph. Ch.</i> , 1895, 18, 107
Ethyl iodide . .	41.3°	41.9	
Propyl alcohol	94.8°	15.8	
Isobutyl alcohol	104.6°	19.4	
Isoamyl alcohol	131.5°	25.75	
Methyl formate	32.3°	15.05	
Ethyl formate	53.8°	21.8	
Methyl acetate	56.5°	20.6	
Ethyl acetate . .	75.5°	27.9	
Methyl propylketone	102°	31.4	
Ethylene chloride . .	82.3°	31.2	
Ethylidene chloride . .	57°	32	
Menthol . . . . .	212°	61.5	
Menthone . . . . .	206°	21.8	
Camphor . . . . .	204°	60.9	
Naphthalene . . .	21.8°	58	<i>Z. physikal. Chem.</i> , 1914, 89, 111
Acetic acid . . .	118°	29.9	Beckmann, <i>Zs. Ph. Ch.</i> , 1906, 57, 129
Propionic acid	139.6°	35.1	"
Butyric acid . . .	163.2°	39.4	"
Methyl alcohol	67°	8.8	Paal, <i>Ber. Chem. Ges.</i> , 1892, 25, 1234
Formic acid . . .	101°	34.2	Cuisa, <i>Gazz. Chim.</i> , 1911, 41a, 688
Amyl acetate . . .	142°	48.3	Beckmann, <i>Zs. Ph. Ch.</i> , 1907, 58, 543
Methylal . . . . .	41°	20.4	
Methyl sulphide	37.5°	18.5	Werner, <i>Zs. anorg. Chem.</i> , 1897, 15, 1
Ethyl sulphide	91°	32.5	
Aniline . . . . .	184°	32.2	Beckmann, <i>Zs. Ph. Ch.</i> , 1891, 8, 223
Cyclohexane . . .	81.5°	27.5	Muscarelli and Musalty, <i>Gazz. Chim.</i> , 1911, 41a, 80
Quinoline . . . . .	232	56.1	Beckmann, <i>Zs. anorg. Chem.</i> , 1906, 51, 237
Nitro-benzene . .	205°	50.4	Biltz, <i>Mon. Chem.</i> , 1901, 22, 627

For 1 mol. of solute in 100 gram of solvent.

Solvent	Boiling-point	Ebulli- scopic Const.	Reference
Piperidine . . . . .	105°	28.4	Werner, <i>Zs. anorg. Chem.</i> , 1897, 15, 1
Benzonitrile . . . . .	191°	36.5	"
Acetonitrile . . . . .	80.5°	17.3	Bruni and Salu, <i>Gazz. Chim.</i> , 1904, 34b, 481
Phenol. . . . .	183°	30.1	R. Meyer and Jager, <i>Ber. Chem. Ges.</i> , 1903, 36, 1555
Thymol . . . . .	230°	68.2	"
Fenchone . . . . .	192.5°	59.4	Runini and Olivari, <i>Gazz. Chim.</i> , 1907, 37b, 229
Pyridine . . . . .	111.5°	27.1	Walden and Centnersagwer, <i>Zs. Ph. Ch.</i> , 1906, 55, 324
Carbon tetrachloride. . . . .	78.5°	48	Beckmann and Stoch, <i>Zs. Ph. Ch.</i> , 1895, 18, 107

*Beckmann Apparatus.* One form of Beckmann's apparatus is shown in Fig. 12 (XIII). It consists of a three-necked flask with a piece of thick platinum wire sealed through the bottom. The bulb is half-filled with glass beads, which, with the platinum wire, promote steady boiling and tend to prevent local overheating. The centre neck carries a condenser fitted with a guard tube containing calcium chloride, and the lower end of the condenser passes down into the solvent at a point remote from the bulb of the thermometer. A small hole in this tube near the top of the flask allows the vapour to pass into the condenser. The thermometer passes through the shorter of the two side-tubes, while the longer serves for the introduction of the solute. The flask containing the beads but without the condenser and thermometer is corked and weighed to 0.01 gram; solvent is introduced to fill the bulb nearly two-thirds full and the weighing is repeated. An asbestos jacket is then placed on the flask, the thermometer and condenser fitted, and the flask gently heated with a small flame so that the solvent drips from the condenser at the rate of about 6 drops per minute. The boiling is continued for about 40 minutes to remove all dissolved gases, and then the reading of the thermometer is taken at intervals of 5 minutes, tapping the thermometer before each reading to prevent the mercury sticking. When the temperature has become constant, which may take a long time, the solute is added through the side-tube and readings are again taken until they become constant. Further quantities of the solute may be added and the readings repeated. Solids are usually made into small tablets by means of a steel press before weighing. Liquids are weighed in a pipette supplied with the apparatus, and after the liquid has been introduced the weight added is found by reweighing the pipette.

*Improved Form of Beckmann Apparatus.* An improved form of Beckmann apparatus is shown in Fig. 13 (XIII). Here the test-tube containing the solution is surrounded by a glass or porcelain jacket containing boiling solvent and fitted with a condenser, so that the tube is surrounded by a jacket of vapour. The inner tube is prevented from touching the jacket by a layer of asbestos paper at the bottom. The jacket contains some pieces of porous tile to promote regular ebullition. The inner tube has a stout piece of platinum wire sealed through the bottom. This tube is fitted with corks and weighed; 20 ml. of solvent are added and the tube weighed again. The thermometer is fixed in position and glass beads, garnets or platinum tetrahedra are added so as completely to cover the bulb of the thermometer and to come about half-way up the liquid. The condenser having been inserted, a piece of asbestos paper is wrapped round the lower

end of the test-tube and this is fitted into the jacket, which contains 20 ml. of the solvent, and the jacket is placed on the stand. The stand is made of asbestos board and is heated by two Bunsen burners placed in the two corners opposite the asbestos chimneys. The heat passes chiefly to the jacket, the central tube being mainly heated by radiation therefrom except in the case of liquids of high boiling-point, when a small flame is placed directly under the central tube. Measurements are carried out in the manner already described. A small correction of from 0.2 to 0.35 gram, according to the boiling-point of the solvent, may be applied to the weight of the solvent to allow for that which is in the condenser, &c. The steadiness

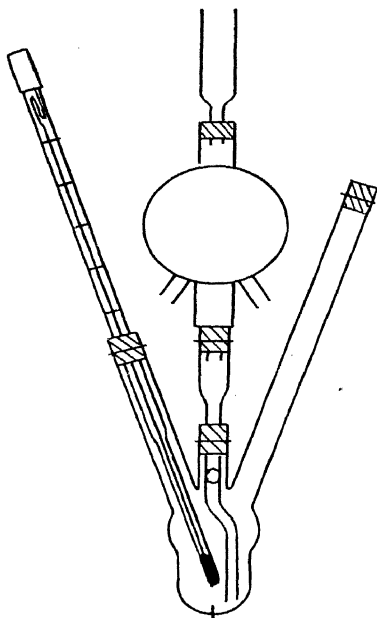


FIG. 12 (XIII)

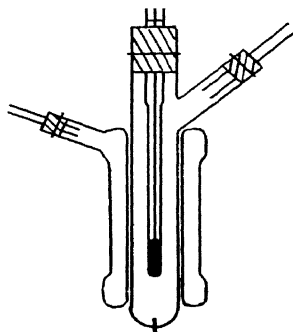


FIG. 13 (XIII)

of the thermometer reading is much improved by surrounding the thermometer bulb with a cylindrical shield of platinum.

Another form of accurate boiling-point apparatus is shown in Fig. 14 (XIII). This form is made by Hanff and Buest (Berlin) and has been used by Reilly and Buckley. It consists of an inner cylindrical boiling tube containing a heating coil of wire which holds the solvent and the lower half of the tube projects into a hollow vessel also cylindrical and containing the same liquid. The boiling tube has two limbs, the longer one has an inner condenser and erect valve; the shorter limb is wider near the main tube joint and is used to introduce the solute. It is lagged with cotton wool upwards from its waist, where it fits the outer tube, and along each

limb. A Beckmann thermometer introduced through the top stopper reaches almost to the heating coil. The outer vessel is hollow so as to fit over the boiling tube and the solvent it contains is refluxed in a side limb similar to the longer limb of the boiling tube. An airtight chamber is made when the boiling tube is pushed into the outer tube. The heating is by an oil bath which boils the solvent in the outer jacket, and the air in the air-chamber is thus maintained at the temperature of the boiling solvent. Electrical heating is essential to raise the solvent in the boiling tube to boiling and to further increment the temperature when the solute is introduced. In a particular experiment using water as a solvent, 25 ml. were

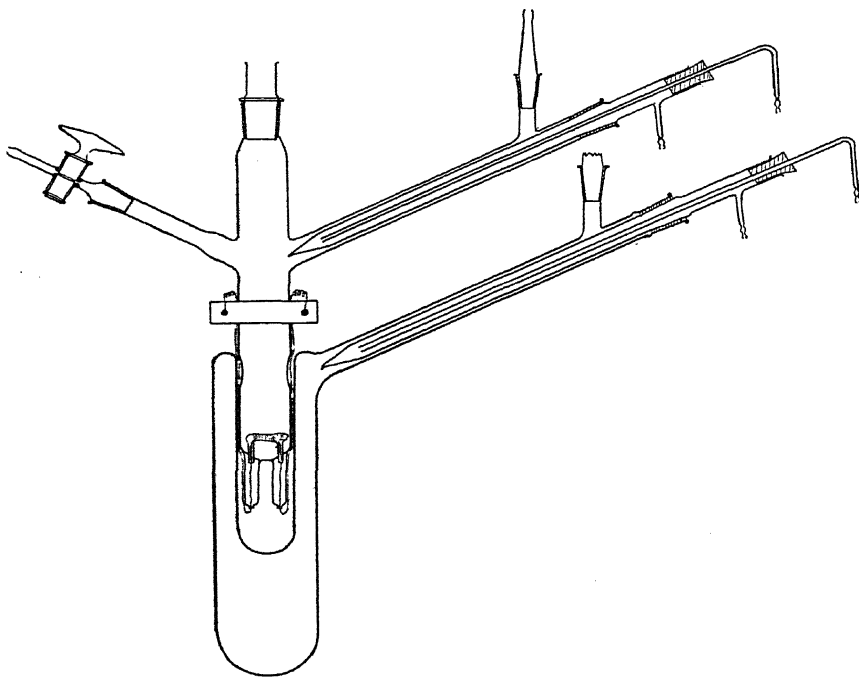


FIG. 14 (XIII)

introduced into the boiling tube and the oil-bath was maintained at  $110^{\circ}$ . This pre-heating continued for more than an hour when the solvent in the boiling tube reached about  $90^{\circ}$ . A current of 1.5 amp. then sufficed to heat the solvent to the boiling-point. The current was switched off momentarily while the solvent was being introduced. A concentration of solute of 1 per cent in solution was arranged and readings of the Beckmann were taken before and after introducing the solute. A steady barometer during the experiment is necessary.

*Other Modifications.* A form of the apparatus adapted for electrical heating is shown in Fig. 15 (XIII). The place of the outer jacket is taken by a Dewar vacuum flask from which the silvering has been removed on

opposite sides to form a window. The current is led in by the thick copper leads shown and heats the small platinum spiral at the bottom. Beckmann has described a further modification of his apparatus (Fig. 16 (XIII)), in which the solution is heated by a current of the vapour of the solvent. The boiling tube A is provided with an internal tube D fused in at the side and passing to the bottom. The boiling tube is sealed to the other tube C at a point above the opening of the inner tube. The tubulus R is for the addition of solvent to the outer vessel and contains a safety valve. Vapour passes from the outer jacket through the tube D into the solution contained in A.

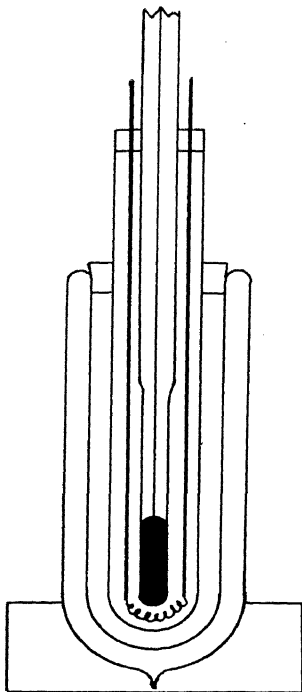


FIG. 15 (XIII)

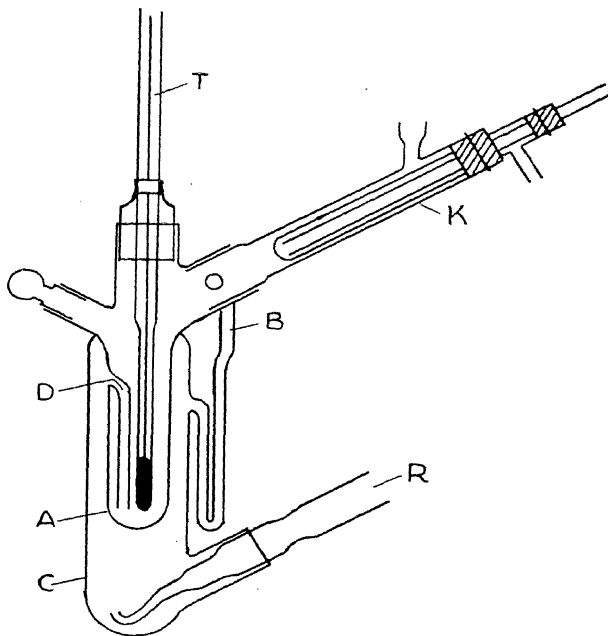


FIG. 16 (XIII)

The condensed vapour may be allowed to flow back into A, or by turning K so as to bring the hole therein opposite the end of the tube B, it may be returned to the jacket. The volume of the solution is read off from the graduations on A. Sakurai also describes a method in which the solution is heated by means of the vapour of the solvent. The boiling vessel (Fig. 17 (XIII)) is a U-tube 21 cm. high and 2 cm. internal diameter, with a side-tube for connecting to the condenser. The solvent is boiled in an ordinary round-bottomed flask enclosed in a tinplate jacket to shelter it from draughts, and the vapour is led by a glass tube to the bottom of the U-tube. The latter is enclosed in a box of asbestos board, the bottom being



either plain asbestos board with low boiling-point solvents, or having a small hole in it. Glass beads fill the end of the U-tube; solvent is poured

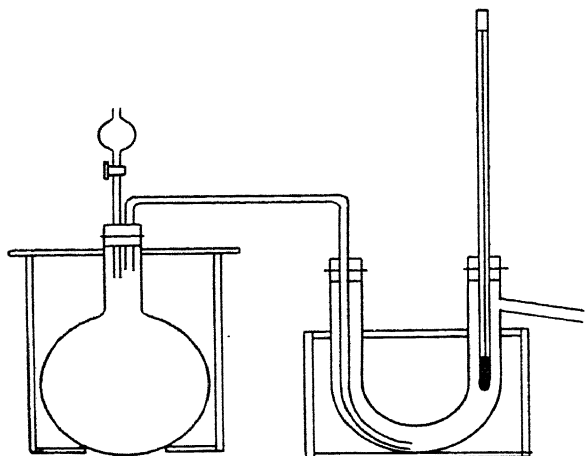


FIG. 17 (XIII)

in to a height of 3 or 4 cm. above the beads and the thermometer is inserted. The gas supply to the burners is adjusted so that the volume of solvent in the U-tube remains constant and the readings of the thermometer are taken until a constant boiling-point is obtained. The solute is then added and the boiling-point obtained in the same way.

*Differential Method.*

Barnes, Archibald and McIntosh use a differential method with two platinum-resistance

thermometers of equal resistance, and each made of 1 metre of 0.15 mm.

wire wound on a mica frame. The thermometers were sealed into glass tubes and then again into wider tubes containing glass beads and the solvent: the two tubes were heated in an air or oil-bath and when both were boiling freely the zero-point on the bridge was determined. A weighed quantity of the solute was added to one tube, and the change of resistance and so the difference of temperature was determined. The composition of the solution was found by analysis. When the elevation of the boiling-point is very small it is often an advantage to use a platinum resistance thermometer instead of the ordinary Beckmann. Thus Linstead and Lowe<sup>1</sup> found that in the ebullioscopic method boiling naph-

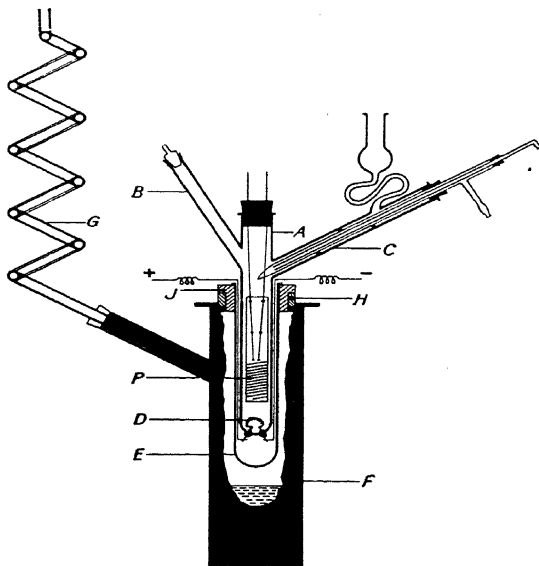


FIG. 18 (XIII)

<sup>1</sup> *J. Chem. Soc.*, 1934, 145, 1031.

thalene dissolved only 0.4 per cent of magnesium phthalocyanine and the maximum elevation with this substance was  $0.04^{\circ}$ . The very delicate platinum resistance thermometer employed by them was made from 48 cm. of platinum wire 0.002 inch in diameter wound on thin mica. Fig. 18 (XIII) gives the general set-up of the apparatus. The leads were of silver wire and the measurements carried out by means of a standard Callendar-Griffith's bridge. The thermometer was mounted by means of a moulded asbestos stopper in the inner tube A, of Pyrex glass, which was fitted with two side arms B for the introduction of the solute and C for the condenser and drying tube. Most of the heat required to keep the solvent in A boiling was provided by an outer jacket containing the vapour of boiling naphthalene and the additional heat by a resistance D.

*Landsberger Method.*

Walker and Lumsden describe a modification of Landsberger's method, in which the volume of the solution is determined instead of the weight. The apparatus is shown in Fig. 19 (XIII). The outer tube E is connected to a condenser C. The vapour of the solvent passes through R into the inner tube N, which is graduated in millilitres and is provided with a small hole at H to allow the vapour to pass into the outer jacket E. 12 ml. of solvent are placed in N and vapour passed in

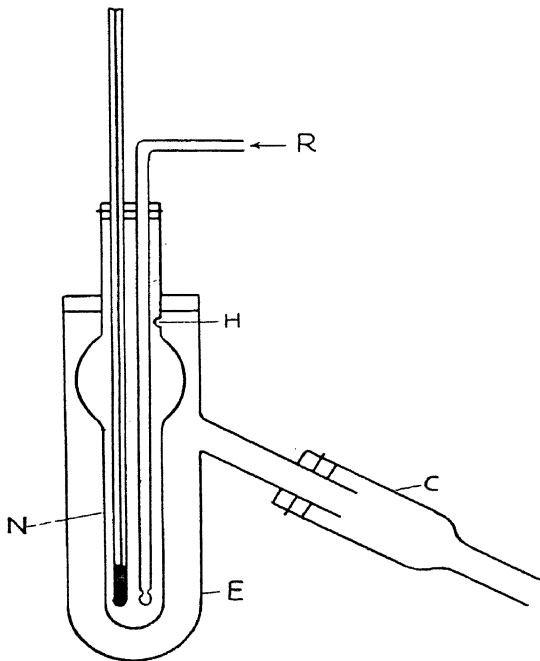


FIG. 19 (XIII)

until it drops from the condenser at the rate of at least one drop in 2 seconds. The thermometer is then read and the heating stopped. The method of heating the solvent in N obviously precludes superheating. The solvent is then poured out until about 6 ml. remain and from 0.5 to 1 gram of the solute are weighed and added. Vapour is then passed in at the same rate as before and the thermometer again read. The flask containing the solvent is at once disconnected, the tube R and the thermometer T are removed, the tube N is placed in a glass cylinder which just fits it and holds it vertically, and the volume is read off. The tube is then again fitted to the apparatus, vapour again passed, and a new set of readings taken at the greater dilution. Then

$$M = \frac{K \cdot W}{\Delta T \cdot V \cdot \rho}$$

$g$  being the specific gravity of the solvent at its boiling-point and  $W$  the weight of solute used. A thermometer graduated in tenths of a degree is used, and the determinations are quickly made and are of sufficient accuracy for many purposes.

Erdmann and Unruh dispense with the vapour jacket in Walker and Lumsden's apparatus by using a vacuum flask as jacket.

Turner's modification of the Landsberger apparatus is shown in Fig. 20 (XIII). Glass joints are used so that the apparatus can readily

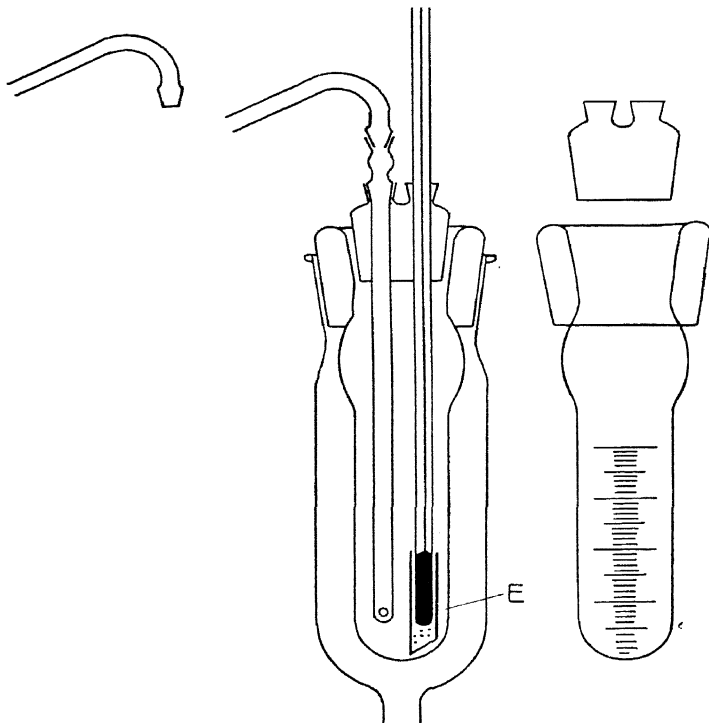


FIG. 20 (XIII)

be detached and the measuring tube weighed. The parts of the apparatus are sufficiently indicated in the diagram. The tube *E* is pierced with a number of small holes and envelops the thermometer bulb to prevent the vapour coming in direct contact with it. The solvent is boiled at a constant rate, e.g. by Sakurai's device of connecting one gas tap to a large and a small burner, both of which are lighted, but the small one alone, which can be regulated independently, being used to heat the flask.

*McCoy's Modification.* McCoy modified the apparatus shown in Fig. 19 (XIII) by combining the vapour jacket and boiling tube as shown in Fig. 21 (XIII), where corresponding parts are similarly lettered. The

solvent is placed in E and the vapour then passes by the tube R into the solution contained in N and, after passing through this, goes by way of the tube H to the condenser C. The solution in N can be heated in the first instance without increasing its volume by opening the clip K, whereby the vapour leaves without passing through the solution.

*Menzies' Method.* Menzies describes a method in which the apparatus shown in Fig. 22 (XIII) is used. This consists of a jacket A in which the solvent is boiled, attached to the reflux condenser B and to the inner test-tube C. D is a clip on the rubber connexion to the condenser and T is a

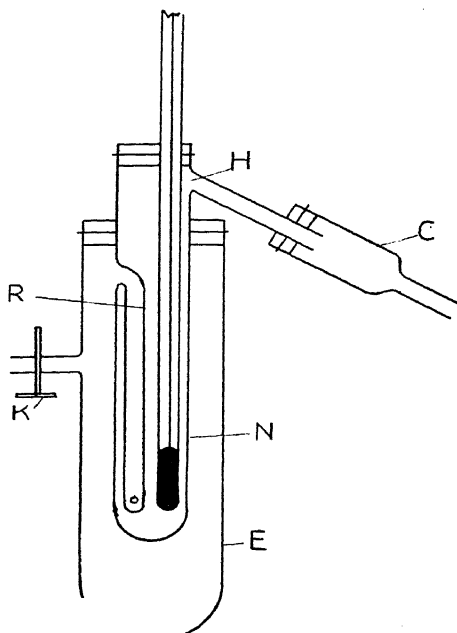


FIG. 21 (XIII)

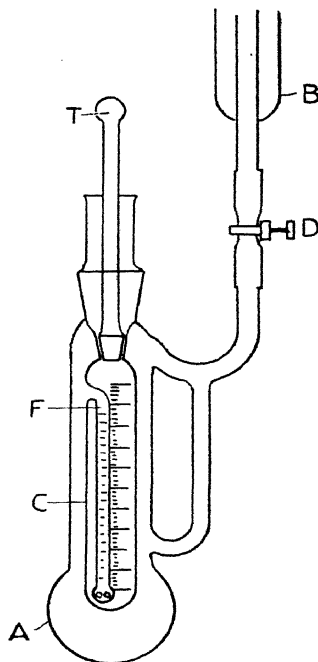


FIG. 22 (XIII)

glass stopper closing the test-tube C. The latter has a pressure-gauge tube F graduated in millimetres, while the test-tube is graduated in millilitres. In making a molecular-weight determination the bulb of the jacket is filled two-thirds full of the solvent, the empty test-tube with the stopper in position is put in, and the liquid is boiled with a small naked flame for 10 minutes under the reflux condenser in order to drive out dissolved gases. The test-tube is then removed, filled two-thirds with the boiled-out solvent and put back without its stopper. The liquid in A is boiled for 1 minute to expel air, the clip D is closed so that the vapour bubbles through the solvent in C and so expels air therefrom. The stopper is then placed loosely in the tube, and when it has warmed is pushed home and the clip is opened. A few drops of

solvent will have condensed in the tube above the stopper and so have made an airtight joint. The apparatus is now allowed to stand for a few minutes to allow the liquid to fall to the boiling-point under atmospheric pressure, and the difference of level of the liquid in the gauge-tube and the test-tube is read and taken as the zero reading. If the solvent is pure this reading will be the same as it was before the stopper was inserted: if not, the blowing-through process is repeated. The weighed solid is now introduced into the test-tube, preferably in the form of a pastille, and the blowing-through repeated to assist in the solution of the solid and to remove air. The apparatus is allowed to stand for 10 minutes with occasional shaking, the liquid in A being continuously boiled, and the difference in level is again read. After removing any liquid above it by means of filter paper the stopper is removed and the volume of the solution in C read off. Further measurements may be made by adding more solvent to the test-tube and repeating the blowing-through. Now  $p_0 - p$  in mm. of solution

$$m \cdot 760 \cdot 13.6 \\ - 1,000 \cdot (\rho - \sigma) = K$$

where  $m$  is the molecular weight of the solvent as gas

$\rho$  is the density of the solution and

$\sigma$  is the density of the vapour at 760 mm. pressure

The molecular weight of the dissolved substance

$$M = \frac{1,000 \cdot W \cdot K \cdot B}{760 \cdot L \cdot V}$$

where  $W$  is the weight of solute

$B$  is the barometric height

$L$  is the lowering of pressure in mm.

$V$  is the volume of the solution in ml., and

$K$  is the constant for which values are given below:

Benzene	.	.	.	.	.	.	.	$K = 1,214$
Alcohol	.	.	.	.	.	.	.	871.5
Water	.	.	.	.	.	.	.	202.5
Chloroform	.	.	.	.	.	.	.	620.4
Acetone	.	.	.	.	.	.	.	1,061
Ether	.	.	.	.	.	.	.	1,577
Carbon disulphide	.	.	.	.	.	.	.	526.6

*Ludlam's Method.* Ludlam describes the apparatus shown in Fig. 23 (XIII). The flask A is half-filled with the solvent and is gently boiled. The vapour passes to the neck of the flask round the tube B and through the small hole G into the space between B and C. Then it descends to the valve  $v$ , consisting of a small glass bead  $w$  sealed to a platinum wire, and so into the tube C and away to the condenser. In about 15 minutes the temperature of the solvent which has condensed in C will have become constant, and is read. The thermometer is then raised above the level of the liquid, the bulb A is touched with the hand, which instantaneously stops the vapour bubbling through C, and the volume is read, the valve  $v$  preventing the liquid from running back into B. A thermometer graduated in tenths of a degree is used.

*Cottrell's Apparatus.* Cottrell<sup>1</sup> pointed out that even if superheating is overcome the temperature indicated by a thermometer bulb immersed in a boiling solution may be as much as  $0.1^\circ$  above the boiling-point at atmospheric pressure on account of hydrostatic pressure. He places the bulb of his thermometer in the gas phase and causes the boiling of the liquid to pump the solution up in such a way as to cover the bulb with a thin film: the constancy and correctness of the thermometer reading is therefore greatly improved, so that it now becomes of greater importance to note and allow for changes in the barometric pressure. Cottrell's apparatus, as modified

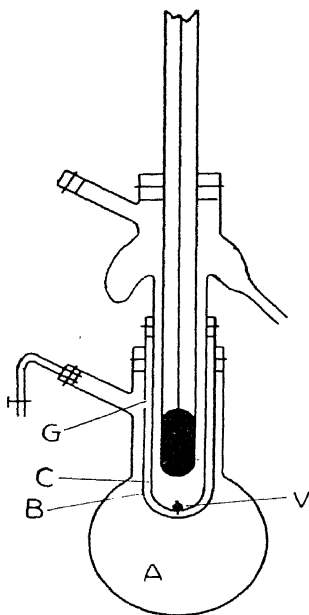


FIG. 23 (XIII)

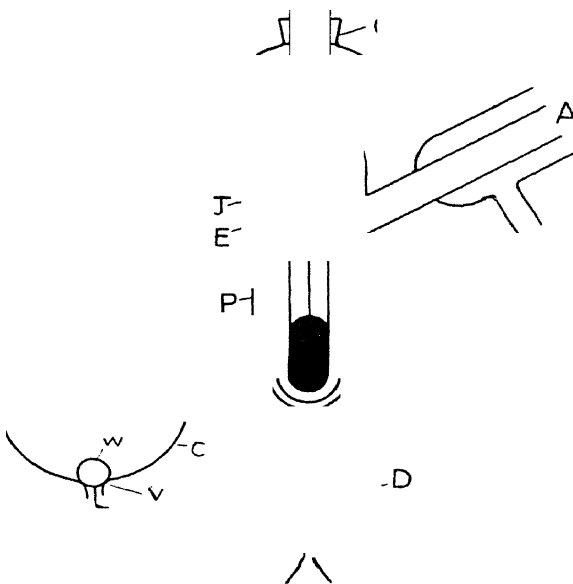


FIG. 24 (XIII)

by Washburn and Read, is shown in Fig. 24 (XIII). The apparatus is constructed entirely of glass, the thermometer being cemented into the ground-glass stopper G. J is a glass sheath carried on the stopper G and protecting the bulb from the cold liquid falling from the condenser A. The pumping apparatus PP is also attached to the stopper. While the solution boils the bubbles of vapour carry solution up to the tube D and squirt it over the thermometer at E. Porous porcelain was used to promote quiet ebullition, and the whole apparatus was protected from draughts by a sheet of asbestos paper. To allow for variation in boiling-points, due to alteration of the barometric height, an apparatus was used on each side; first with

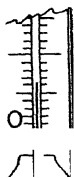
<sup>1</sup> *J. Amer. Chem. Soc.*, 1919, 41, 721.

solvent alone in both, then with solution in one and solvent in the other. The concentrations were determined by withdrawing portions of the solution by means of a side-tube (not shown). This apparatus is an improvement on that of Beckmann.

*The Beckmann Thermometer.* In many of the boiling-point and freezing-point methods the temperature changes are very small and are therefore measured with a Beckmann thermometer. On this instrument the degrees are Centigrade degrees divided into tenths and hundredths, so that thousandths of a degree can be estimated. In order that the hundredth of a degree division shall be sufficiently large to allow it to be subdivided into tenths by eye estimation, it is found possible to have a scale of  $6^\circ$  only on a thermometer about 50 cm. long. To cover the ordinary range of boiling-points and freezing-points used in the laboratory, the Centigrade temperatures indicated by a point on the scale are adjustable by means of a small excess of mercury contained in a reservoir A at the top (Fig. 25 (XIII)). Supposing the thermometer is to be set for a boiling-point determination, the boiling-point of the solvent—let this be  $t^\circ$ —should be indicated by about 1.0 on the scale; if the mercury were to rise to  $a$  the temperature would be about  $6^\circ$  above the boiling-point  $t^\circ$ . A bath is therefore maintained at this temperature,  $t + 6^\circ$ . The thermometer is inverted and given a sharp jerk to force the mercury in A from  $b$  to  $a$ ; the thermometer is next turned carefully up and the bulb placed in the bath, the mercury then expands and may reach  $a$  and so connect up to the reserve of mercury. If it does not do so it must be placed in a bath at a higher temperature until the connexion is made. The thermometer is then placed in the bath at  $t + 6^\circ$ , and after a minute is removed and given a sharp downward jerk which breaks the thread at  $a$ . On cooling to the temperature  $t^\circ$  the mercury should fall to somewhere near the division marked 1.0 on the scale. For a freezing-point determination, where the solvent freezes at  $t^\circ$ , we want the mercury at about the fifth division when the temperature is  $t^\circ$ , so that it will be at  $a$  when the temperature is about  $t + 2^\circ$ . The bath is therefore maintained at this temperature, and after the mercury column has been joined up to the reserve supply of mercury in the reservoir, the procedure which is described above is followed. The thermometer should be set at least 24 hours before it is to be used. Before taking a reading the thermometer should always be tapped with a pencil to prevent the mercury sticking in the narrow capillary tube; an electro-magnetic device is sometimes used to tap the thermometer continuously.

FIG. 25 (XIII)

Owing to the risk of mercury freezing, at lower temperatures other liquids must be used in the thermometer. The addition of thallium to the mercury to make an 8.5 per cent mercury thallium mixture gives a liquid that does not solidify until a temperature of  $-60^\circ$  is reached. Liquid pentane thermometers can be used for temperatures as low as  $-100^\circ$ .



*Determination of Molecular Weights using Small Quantities of Substance.* Pregl has modified the boiling-point method so that it can be carried out using only 10 milligrams of the substance under test and 1.5 ml. of solvent. A small boiling-vessel similar in shape to the larger one usually employed is provided and this is carefully heated in a current of hot air. A specially designed tablet press is also employed. Owing to the great reduction in the quantity of solvent taken a suitable rise in boiling-point is obtained in spite of the minute amounts of solute added.

The technique employed by Pregl is highly specialized and cannot be given in detail here. His book should be consulted when any kind of analytical determination is undertaken on an organic substance available only in small quantities.

**Differential Vapour Pressure Thermometer.** In the Beckmann method and its modifications there still remains (1) the inherent errors of the Beckmann type of thermometer, (2) the uncertainty as to the concentration of the solution at the moment when the boiling point is measured due to the fact that some of the solvent is in the vapour state and some present on the walls of the apparatus above the solution, and (3) the difficulty introduced by the alteration of the boiling-point produced by a change of the barometric pressure during the course of the experiment.

These difficulties are overcome by the use of the differential thermometer of Menzies, this (Fig. 26 (XIII)) has two bulbs connected by a narrower tube about 10 cm. long; the lower end of the tube carrying one bulb is bent upwards so that this bulb lies alongside the lower end of the stem. The glass is carried upwards beyond the upper bulb and is expanded at the top so as to give a diameter large enough readily to be fixed in a clamp. The thermometer contains a liquid having an appreciable vapour pressure at the temperatures at which the instrument is to be used, for example, water is a convenient liquid for many purposes.

The stem and the lower bulb are marked in centimetres with subdivisions. If the instrument is clamped in a vertical position and both bulbs are at the same temperature the water will stand at a different height in the lower bulb and the narrow tube, owing to capillarity; this reading is taken as the zero. If one bulb is at a different temperature from the other the difference of vapour pressure causes a change in the heights of the liquid in the instrument; the magnitude of this change serves to determine the difference of temperature of the two bulbs. An alteration of the height of the water column of 1 mm. corresponds to a temperature difference of  $0.0313^{\circ}$  at  $35^{\circ}$  and  $0.0026^{\circ}$  at  $100^{\circ}$ . Menzies and Wright<sup>1</sup> describe an apparatus for the determination of molecular weights by the rise of boiling-point, using the differential thermometer.<sup>2</sup> This is shown in Fig. 27 (XIII).

The bulb at the bottom is narrowed at the neck and then expands to a second bulb above which is a cylinder narrowed at the top to form the inner

||

FIG. 26  
(XIII)

<sup>1</sup> *J. Amer. Chem. Soc.*, 1921, 43, 2314.

<sup>2</sup> The complete apparatus is made by Eimer and Amend, New York, and includes a differential thermometer of pyrex glass containing water.



tube of the condenser. Inside the wider cylinder is a second glass cylinder open at both ends which acts as a double jacket. The differential thermometer hangs so that its upper bulb is near the top of the wide cylinder and the lower bulb near the bottom of this: the handle is long enough to provide a projecting piece by which it can be clamped. The pump hangs on the lower bulb of the differential thermometer. The boiling tube is heated directly with a small Bunsen flame, protected by a metal wind shield. Boiling causes bubbles of vapour to pass up the tube of the pump, carrying with them some of the solution, which is thus sprayed over the lower bulb of the thermometer; the upper bulb is in the vapour space, and by condensation of vapour very quickly acquires the temperature of the boiling-point of the solvent. Thus, this bulb is at the boiling-point of the pure solvent while the other bulb is at the boiling-point of the solution, and the difference of these two temperatures is the rise of boiling-point required. Equilibrium is reached very rapidly and the apparatus is not sensitive to the disturbing effects of draughts.



FIG. 27  
(XIII)

The concentration of the solution is obtained by having the narrow neck above the lower bulb graduated in millilitres: the volume is obtained by stopping the boiling and taking the reading at once while the apparatus is still full of vapour and the walls are wet with the solvent.

**Determination of the Molecular Weight of Benzil in Chloroform, using the Differential Thermometer.** Clamp the apparatus on the stand at a point below the upper side tube of the condenser at such a height that when the top of the Bunsen is 1 cm. below the bulb its base is several centimetres above the base of the stand. Add purified chloroform (*vide ante*) to reach to the lower graduations on the neck. Turn on the condenser water, light the burner, and adjust the flame by means of a screw-clip. Hang an ordinary thermometer inside the apparatus and take the boiling-point of the pure solvent, avoiding an exposed mercury thread; read the barometer so that if there is any change during the experiment the new boiling-point can be calculated. Lower the Bunsen and swing it aside and, as soon as the boiling ceases, read the volume of the solvent. Resume the heating, remove the mercury thermometer, and insert the pump by lowering it from a hook at the end of a long wire. Put the differential thermometer in position and engage the end of the pump with the lower bulb, then clamp the thermometer in position. While equilibrium is being obtained the pastilles of the solute may be prepared. After about 15 minutes take the zero reading, i.e. the difference in millimetres between the readings on the stem and the lower bulb. In making readings parallax errors are avoided by fitting a white card 10 cm. by 7 cm., on which are bold 1 cm. horizontal graduations, at a suitable distance behind the tube, with the graduations at the same level as those on the tube, and placing the eye so that readings on the card and thermometer correspond. The value obtained for the zero reading is a good check on the purity of the solvent. Any unsteadiness in the position of the thread is due to too slow boiling. Weigh the tube containing the pastilles, drop one in at

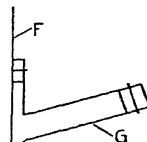
the top of the condenser, and weigh again. As soon as solution is complete the reading becomes constant; read the difference of level and subtract this from the zero reading. Another pastille is then added, and another reading taken for the new concentration.

Since in the present case the volume of the solvent has been determined we require the ebullioscopic constant for 100 ml. of solvent instead of that for 100 grams. This is given in the following table, as is also the temperature difference for 1 mm. change of height in the water column of the differential thermometer at the boiling points given.

Solvent	Boiling-point	K for 1 gm. mol. in 100 ml	Temp. difference for 1 mm.
Acetone . . . . .	56.3°	22.9	0.01215
Benzene . . . . .	80.3°	32.0	0.004918
Carbon disulphide . . . . .	46.3°	19.4	0.01858
Carbon tetrachloride . . . . .	76.8°	32.4	0.005558
Chloroform . . . . .	61.2°	27.7	0.009968
Ethyl acetate . . . . .	77.2°	33.6	0.005480
Ethyl alcohol . . . . .	78.8°	15.8	0.005182
Ethyl ether . . . . .	35.0°	31.1	0.03130
Methyl acetate . . . . .	57.1°	23.4	0.01175
Methyl alcohol . . . . .	64.7°	11.8	0.008692

For accurate work the temperature to which the readings of the differential thermometer are to be referred in order to find the conversion factor to be used is that given by the mercury thermometer, plus half the ebullioscopic rise (found approximately in the first instance); the exact factor is then found from Menzies' table (*loc. cit.*).

4. **The Freezing-point Method**, also due to Beckmann, has the advantage over the boiling-point method that there is no question of super-heating or pressure effect. The same equations used in the boiling-point method apply, *mutatis mutandis*, to the freezing-point method. The apparatus is shown in Fig. 28 (XIII). A weighed quantity of the solvent is placed in A; the stopper, with the Beckmann thermometer F and a platinum stirrer D, is fitted. The tube A is placed in the wider tube B which serves as an air-jacket, and B is placed in the freezing mixture contained in a large battery jar and stirred with a metal stirrer. The freezing mixture must have a temperature of not more than 3° lower than the freezing-point of the solvent. The solvent is weighed out directly into A by fitting this with corks and supporting it in a beaker on the balance pan; 15 to 20 grams, weighed with an accuracy of 0.02 gram, is sufficient. The bulb of the thermometer is placed about half-way down in the solute. An approximate value of the freezing-point is first obtained. The tube A having been placed in B, the solvent is slowly stirred at the rate of about one stroke per second; when solid begins to separate the rate of stirring is increased for a time and then the slower rate is resumed. The mercury will



—B

FIG. 28 (XIII)

increased for a time and then the slower rate is resumed. The mercury will

be found to rise when the faster rate of stirring takes place, and the highest point to which it rises is taken as the freezing-point. The tube A is now removed and allowed to warm in the air with vigorous stirring. When all the solid has disappeared the tube is at once replaced in B and slowly stirred until the temperature falls  $0.1^{\circ}$  below the freezing-point. Freezing is then induced by rapid stirring, and as soon as the temperature begins to rise slow stirring is resumed, the highest point to which the mercury rises being observed, not omitting to tap the thermometer. This procedure is repeated until three readings, agreeing to  $0.002^{\circ}$ , are obtained. The supercooling should be as small as possible and should not exceed  $0.5^{\circ}$ . If the solid does not separate with this degree of supercooling a small crystal of the solid is added by the side-tube G, and for this purpose a small quantity of the solvent is placed in a test-tube immersed in the freezing mixture. The solute, if a solid, is weighed in the form of a pellet, or if a liquid, in the special pipette, and is introduced through the side-tube G. The amount used should be sufficient to give a lowering greater than  $0.1^{\circ}$ . When it has been completely dissolved an approximate value of the freezing-point of the solution is first obtained, and then the more accurate value, in the manner already described for the solvent. Solutions tend to supercool without separation of solid more readily than the solvents, and so it may be necessary to add a crystal of solvent from the small test tube; this is best done by having a rod therein which, when removed, will have a little solid adhering to it. This rod is then inserted through G and the stirrer is raised to touch it, when enough solid will be detached to start crystallization. A second and third determination are made with more concentrated solutions. Solvents such as acetic acid are so hygroscopic that moisture passing in through the aperture through which the stirrer passes is taken up and continuously lowers the freezing-point of the acid. To prevent this Beckmann surrounded the top of the stirrer with a jacket through which dried air was passed, the stirrer being moved by means of a flexible rubber tube.

*Values of Constant for Lowering of Freezing-point.* The values of the constant for some of the more common solvents are:

Solvent	Freezing-point	Cryo-scopic Const.	Reference
Water . . . . .	$0^{\circ}$	18.6	Nernst and Abegg, <i>Zs. Ph. Ch.</i> , 1894, 15, 681
Formic acid . . . . .	$8^{\circ}$	28	Raoult, <i>Ann. Chim. Phys.</i> , 1884, 2, 66
Acetic acid . . . . .	$17^{\circ}$	39	
Nitrobenzene . . . . .	$5.3^{\circ}$	70.5	
Formamide . . . . .	$1.8^{\circ}$	38.5	Bruni and Trovanelli, <i>Rend. Acad. L.</i> , 1904, 13b, 176
Acetamide . . . . .	$82^{\circ}$	40.4	Reilly, Wolter and Donovan, <i>Proc. R.D.S.</i> , 1930, 19, 467
Phenol. . . . .	$38^{\circ}$	74	Eykman, <i>Zs. Ph. Ch.</i> , 1889, 3, 203
o-cresol . . . . .	$30.5^{\circ}$	56.2	Eykman, <i>Zs. Ph. Ch.</i> , 1889, 3, 113
p-cresol . . . . .	$35.9^{\circ}$	77	Eykman, <i>Zs. Ph. Ch.</i> , 1889, 4, 497
Thymol . . . . .	$48.2^{\circ}$	80	
p-toluidine . . . . .	$39.1^{\circ}$	51	
Di-phenyl . . . . .	$70.2^{\circ}$	80	
Di-phenyl methane . . . . .	$26.3^{\circ}$	27	
Benzophenone . . . . .	$48.1^{\circ}$	98	
Urethane . . . . .	$48.7^{\circ}$	51.4	
Anethol . . . . .	$20.1^{\circ}$	63	
p-bromophenol . . . . .	$63^{\circ}$	112	
Stearic acid . . . . .	$61^{\circ}$	45	
Palmitic acid . . . . .	$60^{\circ}$	44	Eykman, <i>Zs. Ph. Ch.</i> , 1889, 3, 203

Solvent	Freezing-point	Cryo- scopic Const.	Reference
Naphthalene	80.1°	69	Auwers, <i>Zs. Ph. Ch.</i> , 1895, 18, 595
Benzene	5.5°	51.2	Paterno, <i>Gazz. Chim.</i> , 1899, 19, 640
Aniline . . . . .	— 5.96°	58.7	Ampola and Rimatori, <i>Gazz. Chim.</i> , 1897, 27a, 35
Di-benzyl . . . . .	52°	72	Garelli and Calzolari, <i>Gazz. Chim.</i> , 1889, 29b, 258
Tri-phenyl methane .	93°	124.5	
Benzylaniline . . . .	36.5°	87	
o-chlorophenol . . . .	7°	77.2	Jona, <i>Gazz. Chim.</i> , 1909, 39b, 289
m-chlorophenol . . . .	28.5°	83	
p-chlorophenol . . . .	37°	85.8	
o-bromo-nitrobenzene	36.5°	91	
m-bromo-nitrobenzene	54°	87.5	
o-nitro benzoic-ester .	30°	74	Bruni and Callegari, <i>Rend. Linc.</i> , 1904, 13a, 567
p-xylol. . . . .	16°	43	Paterno i Montemortini, <i>Gazz. Chim.</i> , 1894, 24b, 197
o-nitro phenol . . . .	44.3°	74	Ampola and Rimatori, <i>Gazz. Chim.</i> , 1897, 27b, 31
Di-methylaniline . . .	1.96°	58	Ampola and Rimatori, <i>Gazz. Chim.</i> , 1897, 27a, 51
p-chlorotoluene . . . .	7°	56	Auwers, <i>Zs. Ph. Ch.</i> , 1902, 42, 513
p-bromotoluene . . . .	26.9°	82.1	Paterno, <i>Gazz. Chim.</i> , 1896, 20b, 1
Cyclohexane . . . . .	6.2°	200	Muscarelli and Benati, <i>Gazz. Chim.</i> , 1909, 37b, 642
Veratrol . . . . .	22.5°	64	Paterno, <i>Gazz. Chim.</i> , 1896, 26b, 9.
Acetophenone . . . . .	19.5°	56.5	Garelli and Montanari, <i>Gazz. Chim.</i> , 1894, 24b, 229
p-toluic phenyl-ester .	32°	62	Auwers, <i>Zs. Ph. Ch.</i> , 1902, 42, 513
Phenyl benzoate . . . .	69°	80	Garelli and Gorni, <i>Gazz. Chim.</i> , 1904, 34b, 111
p-iodotoluene . . . . .	34°	100	Bruni and Padoa, <i>Gazz. Chim.</i> , 1904, 34a, 133
Bromoform . . . . .		144	Ampola and Manuelli, <i>Gazz. Chim.</i> , 1895, 25b, 91
Resorcinol. . . . .	110°	65	Garelli, <i>Gazz. Chim.</i> , 1895, 25b, 173

Some of the solvents are solids at the ordinary temperature, and it will be seen that the constants are very large, so that a thermometer graduated in tenths of a degree may be used instead of the Beckmann. The method of carrying out the experiment is similar to that described, with the exception that the outer vessel C is replaced by a large beaker containing water heated to a constant temperature about 3° below the melting-point of the solvent.

Dioxan has been suggested by Oxford<sup>1</sup> for use as a solvent in the cryoscopic method of determining molecular weights. It is chemically inert and has wide solvent power. Most crystalline organic substances including many natural products other than sugars and amino acids are soluble in it. Its freezing-point is 11.67° and its molecular depression constant is 47.

*Ostwald's Modification.* For more exact determinations Ostwald maintains that 500 to 1,000 grams of the solvent should be weighed out into a cylindrical glass vessel surrounded by a higher and wider metal vessel which in turn is placed in a large bath containing the freezing mixture; the bath is lagged and covered to prevent, as far as possible, heat from passing in. The freezing-point of the solvent is first determined, then a known amount of the solute is added in the form of a concentrated solution after the removal of an equal amount of the solvent. The freezing-point is then again determined. Allowance is made for the amount of solid solvent which separates by a calculation for the degree of supercooling used. If  $C$  is the specific heat of the solution,  $\lambda$  the latent heat of solidification per gram, and  $\theta$  the over-

<sup>1</sup> *Biochem. J.*, 1934, 28, 1325.

cooling, then the fraction of the liquid which solidifies is  $r$ , where  $r = C\theta/\lambda$ ; the concentration of the solution whose freezing-point has been determined is therefore increased from  $p$  to  $p(1 + C\theta/\lambda)$ .

In addition to the solvents already mentioned, Morgan and Benson<sup>1</sup> have used melted crystalline hydrates as solvents; for example, they determined the molecular weight of acetic acid dissolved in melted calcium chloride,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , for which the freezing-point is  $29.48^\circ$ , and  $K$  is  $45.0$ .

The apparatus shown in Fig. 29 (XIII) has been employed<sup>2</sup> also for molecular weight determinations.

Freudenberg<sup>3</sup> working on the molecular weight of triacetylcellulose in

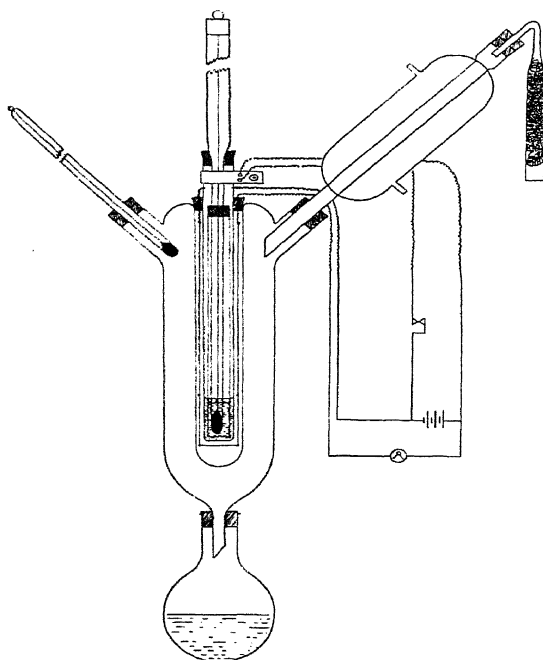


FIG. 29 (XIII)

acetic acid, obtained some remarkable results in experiments at small concentrations, depending upon the procedure employed in the molecular weight determinations of polysaccharides and their depolymerized derivatives. He states that certain low results obtained for molecular weights depended on the degree of supercooling and the delayed speed of crystallization. This is of special importance when small depressions are produced by solution of polysaccharides or non-crystalline substances in the solvent.<sup>4</sup> Freudenberg uses the following method: When melting the crystals of the solvent (e.g. acetic acid) which separate during the molecular weight determination in the cryoscopic method, he raises the temperature only  $0.8^\circ$  to  $1^\circ$

over the melting-point of the acetic acid. In this way a few small crystals of the acetic acid remain unmelted. The temperature is then lowered by the cooling of the outer jacket until the thermometer reads from  $0.05^\circ$  to  $0.1^\circ$  above the melting-point of the acetic acid. Stirring is then commenced by means of the 'make and break' device. In this way the degree of undercooling does not go below  $0.08^\circ$  to  $0.1^\circ$  before the mercury thread ascends,

<sup>1</sup> *J. Amer. Chem. Soc.*, 1907, 29, 1168.

<sup>2</sup> Reilly, Wolter, and Donovan, *Sci. Proc. Roy. Dub. Soc.*, 1930, 19, 41, 467.

<sup>3</sup> *Ber.*, 1929, 62, 3078.

<sup>4</sup> Cf. Standinger and others, *Ber.*, 1928, 61, 2575, on molecular weight of rubber solutions, who also observe delayed crystallization of solvent.

and crystallization of the solvent begins. If the under-cooling is greater than the above limits, the mercury will register a higher figure, owing to the fact that a large number of small crystals (with a corresponding larger surface) are formed, and these serve as a quick-heat supplier ('gute Wärme-Nachlieferung'), and, therefore, the mercury rises more quickly. On the other hand, if the degree of super-cooling is less than the above limits the mercury will give a lower reading, as in this case fewer big crystals will be formed, thereby lessening the heat supply, and thus slowing down the rise of the mercury. In consequence, a very long time is required to reach equilibrium. The temperature of the outside bath, of course, also affects the speed of crystallization since the degree of super-cooling is largely dependent on this external temperature.

The period from the time when the mercury starts to ascend until it reaches its maximum point should be the same in the case of the solvent alone and with the polysaccharide in solution. The same procedure is adopted with the solute in solution as that in the case of the blank or control.

As a result of these observations Freudenberg disputes certain results obtained by Hess in regard to molecular weight determinations of triacetylcellulose in acetic acid. Hess<sup>1</sup> states, however, that determinations are only influenced when the depressions produced by the solute are of a very small order. He attributes the differences in observations by Freudenberg to the following two facts: (1) Freudenberg's acetic acid used had not been purified to such an extent as his solvent; (2) the small under-cooling got by Freudenberg lowers the speed of crystallization, and thereby gives a bigger depression than the actual solute produces.

The following examples illustrate the results obtained in determining the molecular depression constant for acetamide, by Reilly, Wolter, and Donovan. As is usual in molecular weight determinations, the first reading after introducing the substance is generally abnormal, and is omitted in calculating average values:

*Acetanilide (low concentration).*

0.1974 g. Acetanilide, 16.34 g. Acetamide, concentration 1.208 per cent.

Under-cooling	Reading	Time	Under-cooling	Reading	Time
3.55°	3.191°	5 min.	4.25°	5.550°	5 min
3.50°	3.190°		4.30°	3.549°	6 "
3.61°	3.189°		4.27°	3.551°	5 "
Average 3.190°			Average 3.550°		
			— 3.190°		

$$\Delta = 0.360^{\circ}$$

$$K = \frac{M \times \Delta \times W}{w \times 100} = \frac{135 \times 0.360 \times 16.34}{0.1974 \times 100} = 40.2.$$

<sup>1</sup> *Ber.*, 1930, 65, 526.

*Acetanilide (high concentration).*

0.3686 g. Acetanilide, 17.16 g. Acetamide, concentration 2.148 per cent.

Under-cooling	Reading	Time	Under-cooling	Reading	Time
3.29°	3.053°	4 min.	4.09°	3.700°	8 min.
3.23°	3.055°	5 „	4.10°	3.702°	
3.23°	3.055°	5 „	4.06°	× 3.703°	
3.27°	3.056°	4 „			
Average	3.055°		Average	3.702°	
			—	3.055°	
$\Delta = 0.647^\circ$					

$$K = \frac{135 \times 0.647 \times 17.16}{0.3686 \times 100} = 40.7$$

**Adam's Method.** Freezing-point depressions, particularly for very dilute solutions, can be determined very accurately by measuring the difference of temperature between water in equilibrium with ice and solution in equilibrium with ice, using vacuum jacketed vessels. The method has been developed by Adams,<sup>1</sup> Randall and Vanselow<sup>2</sup> and Hovorka and Rodebush.<sup>3</sup> The last author's method is the simplest and will be described here. The apparatus consists of the two silvered Dewar flasks F and G (Fig. 30 (XIII)), which are connected by a thick-walled capillary tube, so that they are maintained at the same degree of vacuum, and which are set in a block of plaster of Paris at the bottom.

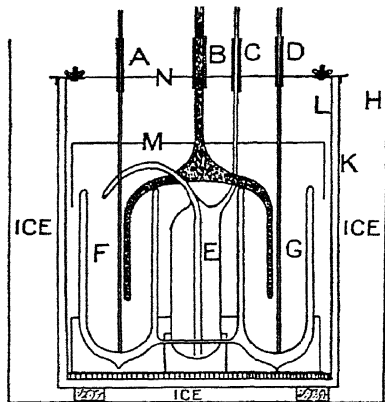


FIG. 30 (XIII)

G is destined to contain ice and water and F ice and solution. The thermocouple B dips into the two flasks and serves to measure the temperature difference. A second single junction thermocouple is connected to the wall at K at one junction, while the other is in F, so that this temperature difference can be measured when necessary; the leads from this thermoelement are carried along the rubber tube C which is connected to the solution vessel E (also set in plaster of Paris). This solution vessel has a tube extending over the top of F for the introduction of solution therein by the application of pressure at C. A cover M of thick paper which has been treated with hot paraffin-wax serves to prevent the introduction of impurities into F and G. The flasks are suspended from the cover N inside the cylindrical copper can K, which is surrounded by the ice in the sheet-metal container H, itself covered with a thick layer of felt. Tube A reaches to the bottom of the Dewar flask F and serves for the withdrawal of solution or for

<sup>1</sup> *J. Amer. Chem. Soc.*, 1915, 37, 480.

<sup>2</sup> *Ibid.*, 1924, 46, 2422.

<sup>3</sup> *Ibid.*, 1925, 47, 1614.

bubbling air. The corresponding tube D serves for air bubbling or for the introduction of water.

**The Thermocouple.** This consists of fourteen junctions, each of which is made from three No. 36 D.S.C. constantan wires, and one No. 35 D.S.C. copper wire. The use of three constantan wires in parallel reduces the effects of irregularities in these wires. The wires should be cut to the required lengths and then coated with shellac. About 3 mm. of the ends of the wires are bared and the junctions hard soldered. The solder consists of three parts brass and one part silver, and the flux is anhydrous borax glass. Use small quantities of solder and flux and a small gas jet from a glass tube. Cover the joints with an insulating varnish made by stirring sublimed (or, better, insoluble) sulphur into a solution of crude rubber in benzene and carbon disulphide until the amount reaches 20 to 25 per cent. Dip the junctions in the varnish, dry in the air, and then heat at  $140^{\circ}$  for 15 hours. Tie the junctions in small bundles with silk thread and then tie the bundles to pieces of thin brass rod to give rigidity. Embed the ends in naphthalene in glass tubes, coat the intermediate portion with melted paraffin-wax (to exclude moisture), and wrap in silk ribbon. Standardize the thermocouple against a standard thermocouple, or by measuring the E.M.F. given between the melting-point of mercury ( $234.2^{\circ}$  K.) and ice ( $273.1^{\circ}$  K.) and the transition point of sodium sulphate ( $305.5^{\circ}$  K.) and ice. It gives about 550 microvolts per degree.

**Determination of the Molecular Weight of Potassium Chloride in Aqueous Solution.** Prepare an N/100 solution of potassium chloride and place it in the container E; cool this in a freezing mixture until ice crystals appear: allow the crystals to melt just before putting E in the container L. Clean the two Dewar flasks and wash them with conductivity water before placing in L. Fix the cover N in position together with A, B, C, and D; and then, through the holes in the sides of L, fill F and G with ice. The ice is cracked in a clean cloth to pieces about 1 ml. in size, then sifted to get rid of the small particles, and washed with conductivity water. Put the assembly in the can H and fill this with crushed ice.

By means of the single element thermocouple determine when the contents of F are within  $0.5^{\circ}$  of the ice surrounding K, and then suck out the water which has collected at the bottom of F by means of the tube A. Allow a little of the solution from E to flow over the ice in F, and remove this solution from the bottom of F. Repeat this washing of the ice three times, so that the solution will not be diluted by water adhering to the ice. Run in solution from E to fill F. By means of D introduce conductivity water, already cooled to  $0^{\circ}$ , into G. Air, purified by bubbling through caustic potash and sulphuric acid, is divided into two streams and passed through water and solution respectively in equilibrium with ice, and then at equal rates by way of A and D into F and G; this stirs the liquids and saturates them with air. After 30 minutes take the first reading of the thermocouple B, bubble the air for a further period of 60 minutes, and again take the reading; if this does not agree with the former, repeat the bubbling until two successive readings do agree. Then take six readings at intervals of 20 minutes, and use the mean value of the E.M.F. to calculate the temperature difference.



Calculate the molecular weight of the potassium chloride and the fraction ionized.

The Hortvet apparatus described in the chapter on Melting-points may also be employed in molecular weight determinations.

**5. Lowering of the Transition-Point.** Lowenherz first investigated the lowering of the transition-point by the addition of foreign substances. He found that the transition-point of sodium sulphate decahydrate into anhydrous sodium sulphate, which is  $32\text{--}38^\circ$ , was lowered by such substances as carbamide, dextrose, &c., by amounts which gave a molecular depression of 32.6 when the concentration of the substance is referred to 100 grams of the decahydrate.

Dawson and Jackson prefer to refer the concentration to 100 grams of solution, a change readily calculated from the equation for the reaction, and giving in this case 28.5 for the molecular depression. Other transition-points are magnesium chloride hexahydrate to tetrahydrate,  $T\ 116\text{--}67^\circ$ ,  $K = 76$ ; rubidium tartrate dihydrate to anhydrous salt,  $T\ 40\text{--}41^\circ$  and  $K\ 37.1$ ; sodium bromide dihydrate to anhydrous salt,  $T\ 50\text{--}7^\circ$  and  $K\ 34.5$ . The apparatus used is that of Meyerhoffer, in which the Beckmann thermometer bulb is surrounded by a rapidly rotating, perforated, cylindrical Witt stirrer, the speed of which is controlled by a rheostat in the motor circuit. The tube containing the thermometer is surrounded by a wider tube immersed in a thermostat maintained at  $3^\circ$  to  $5^\circ$  below the temperature of the transition-point. About 100 grams of the salt are used and heated about  $10^\circ$  above the transition-point until the transition is complete; the system is then under-cooled about  $0.5^\circ$  below the transition-point, a crystal of the new phase is added and the highest temperature to which the thermometer rises is observed. When the transition has been accurately determined a similar experiment is carried out in which a weighed amount of the solute is added to the weighed amount of solvent and the new transition-point is determined. The concentration of the solution is calculated from the equation; for example, with sodium sulphate, since 100 parts of saturated solution contain 33.4 parts of anhydrous salt, the 'equation' may be written:

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 0.367 \text{ Na}_2\text{SO}_4 + 0.100 (100\text{H}_2\text{O}, 6.33 \text{ Na}_2\text{SO}_4)$   
therefore 100 parts of decahydrate give 87.3 parts of solution.

**6. The Lowering of Solubility.** Nernst has shown that the relative lowering of the solubility of a solute in a solvent by the addition of a foreign substance can be used to determine the molecular weight of the foreign substance. Since

$$\frac{L_0 - L}{L_0} = \frac{n}{N + n}$$

where, for example,  $L_0$  may be the solubility of ether in pure water,  $L$  the solubility of ether in the aqueous solution,  $n$  is the number of molecules of the foreign substance, and  $N$  is the number of molecules of ether. Then if  $g/M$  is put for  $n$

$$(L_0 - L)M = \frac{L_0}{N + n} \text{ or in dilute solution } = \frac{L_0}{N} = C \text{ and hence}$$

$$M = \frac{g \cdot C}{L_0 - L}$$

This method has been used by St. Tolloczko. He employs a flask holding about 100 ml. and having a neck 15 cm. long and 7 to 8 mm. internal diameter. The flask is fitted with a well-ground-in stopper to make it ether-tight. The neck is graduated in half-millimetres. A few drops of mercury are put in the flask and this is then filled up to a fixed point on the neck, with water saturated with ether which has been purified by shaking with water seven or eight times and two or three times with mercury. Ether is then added so that the ether column is just 60 mm. long. The stopper is inserted and the apparatus is shaken in a thermostat until equilibrium is attained. The length of the ether column is then read accurately to 0.1 mm. with the aid of a lens. A weighed quantity, 0.03 to 0.1 gram, of a substance of known molecular weight, e.g. naphthalene, is added and the flask again shaken in the thermostat. The addition of the naphthalene lowers the solubility of the ether in the water so that the ether column above the water increases in length; this new length is read off and the data so obtained are used to calculate the constant for the apparatus. As an example, 0.1266 gram of naphthalene altered the length 0.55 cm.; since the molecular weight of naphthalene is 128,

$$C = \frac{(L_0 - L)M}{g} = \frac{0.55 \times 128}{0.1266} = 556$$

A similar experiment carried out with benzene, 0.0655 gram, using exactly the same volumes of ether-saturated water and pure ether, gave a change in the length of the ether column of 0.45 cm. Therefore

$$M = C \cdot \frac{g}{L_0 - L} = \frac{556 \times 0.0655}{0.45} = 81$$

The addition of the mercury promotes the intimate mixture of the two liquids during shaking and a ready separation into two layers on standing.

**7. The Variation of Solubility with Temperature.** Van't Hoff's isochore can be applied to the solubility of a substance which is not too soluble in water in order to get a value for the molecular weight. Writing it

$$\frac{\partial \log s}{\partial T} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{1}{s} \cdot \frac{\partial s}{\partial t} = \frac{Q}{RT^2}$$

where  $s$  is the solubility and  $Q$  the heat of solution per molecule, then

$$Q = \frac{RT^2}{s} \cdot \frac{\Delta s}{\Delta t}$$

and  $M = \frac{Q}{q}$  where  $q$  is the heat of solution per gram. As an example, van't Hoff gives that 100 grams of water dissolve 2.88 and 4.22 grams of succinic acid at  $0^\circ$  and  $8.5^\circ$ . Hence

$$Q = \frac{2 \times 277^2 \times 1.34}{3.55 \times 8.5} = 6,830 \text{ calories per molecule.}$$

The heat of solution per gram is 55, so that the molecular weight becomes

$$M = 6,830/55 = 124$$

### SECTION 3: MOLECULAR WEIGHTS—MICRO METHODS

A microscopical method for the determination of molecular weights has been developed by Barger. This method depends on the fact that equimolecular solutions in a given solvent will have their vapour pressures lowered by the same amount and so will have the same vapour pressure. If two solutions, not having the same vapour pressure, are enclosed in the same vessel, distillation of solvent will take place from that having the lower molecular concentration to that having the higher. If the vapour pressures are the same, no distillation will occur, so that this can be used as a criterion of equality of molecular concentration. In this case if the molecular concentration of one solution and the weight concentration of the second are known, the molecular weight of the second solute can be calculated.

To see whether distillation takes place short lengths of the two solutions are sealed in a capillary tube, the two solutions being separated by an air bubble. The lengths of the columns of solution are then measured under the microscope from hour to hour. A solution of known concentration of the substance under examination is compared in this way with a series of solutions of a standard substance of known molecular weight.

The method has the advantage that the solvent need not be specially pure, and that very minute quantities of the solute are necessary. As standards Barger used cane sugar in water solution and benzil or azobenzene in organic solvents. When the substance examined is colourless it prevents confusion if a coloured substance like azobenzene is used as comparison solute.

**Example of the Determination of the Molecular Weight of Naphthalene with Ethyl Acetate as Solvent and Azobenzene as Comparison Substance.** *Preparation of Solutions.* An approximate idea of the molecular weight is generally available and a convenient concentration to use is about 0.2 molar. In this case that will be about 128 grams in 5 litres or 0.128 gram in 5 ml. Weigh a small bottle and add about 0.13 gram of naphthalene and weigh again to get the exact weight used. Calculate what volume of ethyl acetate is required to give, with the weight of solute found, a solution of the required concentration, and add this volume from a graduated pipette or a 10-ml. burette. Weigh the bottle again and get the weight concentration of the solution.

Next prepare a series of solutions of azobenzene, having 0.20M. as the central concentration; for example, they might be 0.16M., 0.17M. . . 0.24M.: since the molecular weight is 182, 0.364 gram will be required for 10 ml. of solution of 0.20M. concentration. The simplest method is to weigh about 0.3 gram into each of nine bottles and then to calculate what volume of solvent is required in each case: add this volume from the 10 ml. burette and weigh to get the exact molar concentration.

*Preparation of Capillaries.* Take soft glass tubing of 0.5 inch bore and draw it out into capillaries about 2 metres long; the external diameter should be 0.5 to 1.2 mm. Lengths of 20 to 30 cm. are then cut, care being taken that the ends are cut off square. One end of a capillary is closed with the index finger, and the other end is placed in the first comparison solution; release slightly the pressure on the finger and let a length of about 5 cm. of solution enter. Close the end with the finger and turn the tube with the open end uppermost, and by slightly releasing the finger let in a 3-cm. air bubble.

Wipe the outside of the tube and with the finger pressed on the closed end lower the open end into the solution to be examined, and allow 5 cm. of this to enter: draw this into the tube so as to leave about 3 cm. free. Seal the comparison end and draw out the other end to a very fine capillary, using a flame 3 mm. high; break this off till a length of 2 cm. remains; this is then melted in the flame. Then draw out the comparison end and break off the tip; similarly with the finger-nail break off the tip at the solution end and, by tilting the tube, let this run down until the fine point of the capillary is filled, and then seal this tip with the very small flame, and then the other tip. The liquid under examination thus extends right to the end of the tube, so that any increase or decrease in volume will be shown at one end only. A glass strip 17 cm. long and 2 cm. wide is taken and a reference line marked on it in such a position that when the capillaries are attached to the strip, the free ends of the columns of solution of the substance under test are near the line. The line may consist of a black hair or a strip of tinfoil fastened across the glass with canada balsam. The series of tubes which have been prepared are now placed on the glass strip in the correct order, and so that the free end of the drop to be measured is within half a millimetre of the reference line; they are then fixed in position with canada balsam. The glass strip is now placed in a glass dish made from a strip of glass 20 cm. by 4, by fastening four glass rods cut to size along the edges by means of paraffin-wax. The dish is filled with water, which not only keeps the temperature steady, but also improves the optical definition. The dish is placed on the stage of the microscope: using a magnification of about 100 and a micrometer eye-piece, after 10 minutes the first reading is taken; the distance of each meniscus of the solution under test is measured from the reference mark. After from 3 to 12 hours these readings are repeated; at one end of the series the column of test solution will be found to increase in length while at the other they decrease: so it will be possible to find two neighbouring tubes one of which shows a slight increase and the next a decrease: the molecular concentration of the substance under test is then between those of the corresponding comparison solutions. If desired, a further series of tubes between these limits can be set up and the exact point narrowed down still further: an approximate estimate of this point can be made from the amounts of the changes in length in the two cases; this can best be seen by an example: the first line gives the normality of the comparison solution, the second line the series of readings on the micrometer scale taken at the start; the third line the micrometer readings after 12 hours, and the last line the change in the reading.

0.1M.	0.3M.	0.4M.	0.5M.	0.7M.
- 40	- 49	- 38	- 37	- 21
+ 100	0	- 21	- 56	- 90
+ 140	+ 49	+ 17	- 19	- 69

The normality of the naphthalene solution obviously lies between 0.4 and 0.5, and the gain of 17 on one side and the loss of 19 on the other show that the value will not be very far from 0.45. A second series then gave the following results :

0.42M.	0.44M.	0.46M.	0.48M
- 25	- 30	- 17	+ 1
- 1	- 26	- 17	- 24
+ 24	+ 4	0	- 25

this gives the normality of the solution as 0.46 and since it was made up to contain 57.6 grams per litre of naphthalene we have that

0.46M. solution contains 57.6 grams per litre, therefore

1.00M. solution contains  $57.6/0.46$  grams per litre = 125 (theory 128)

In 1912 attention was drawn to the application of camphor for molecular weight determination.<sup>1</sup> Later it was shown that with an ordinary thermometer it could be employed for such work.<sup>2</sup> And a figure 498 was deduced for the molecular lowering of camphor. This figure is much higher than that afterwards employed by Rast, but it is in good agreement with an indirect calculation. From van't Hoff's relation the latent heat of fusion of camphor is 8.24 calories. Calculated from the vapour pressure determination of camphor by Ramsay and Young, combined with a knowledge of the specific volumes of camphor in the liquid and solid states, a value of the latent heat of fusion is obtained, identical with that deduced from van't Hoff's equation.

Since camphor melts at 174° the method is not applicable to substances which decompose lower than 180°. Again, melted camphor contains both the keto and enol forms, so that the substance used must be soluble in camphor but at the same time must not react with either form.

The camphor method of Rast,<sup>3</sup> which has been widely used in micro-work in recent years, depends on the extraordinary great freezing-point depression constant of camphor (40° for one gram molecule of dissolved substance in 1 kg. camphor), which allows the molecular weight of a substance to be determined from a simple observation of the 'mixed' melting-point of the substance and camphor, taken with an ordinary accurate thermometer. With substances of fair solubility in molten camphor (e.g. 10 per cent) and average molecular weights, a freezing-point depression of about 8° to 20° is obtained : but, as has been noted by Pregl, the method is obviously limited for many substances by their low solubility in camphor.

Ten mg. of the substance under examination are mixed with 100 mg. of camphor. The melted mixture, when clear, is then allowed to solidify. The next operation consists in breaking up this material, and part of it is placed in a small melting-point tube as in the carrying out of an ordinary melting-point determination (see the chapter on this subject), and the melting-point

<sup>1</sup> Jouniaux, *Bull. Soc. Chim.*, 1912 [4], 11, 546 ; also see Le Fevre (*Nature*, 1930).

<sup>2</sup> *Ibid.*, p. 722.

<sup>3</sup> *Ber.*, 1921, 55, 1051.

determined in the usual way. The difference from the original camphor is the 'depression'. The method is claimed to be accurate to within 5 per cent. When more of the substance is available the following method may be used in which a determination of the Freezing Point Depression Constant precedes the actual Molecular Weight Determination: this is desirable because the value found by slightly different technique is somewhat variable, while an individual observer can get very consistent results by following exactly his own procedure on each occasion. Rather larger capillary tubes (10 cm. long by 2–3 mm. diameter) are used. Some pure camphor is ground to powder with a spatula on an unglazed porcelain plate and is put into the capillary and pressed down with a glass rod so that the column is about 15 mm. high. The camphor is melted, using the ordinary melting-point apparatus, to give a clear liquid and the temperature of the bath is then allowed to fall till solidification is complete. The heating of the bath is resumed at the rate of not more than  $1^{\circ}$  per minute and the temperature taken when the last trace of crystals disappears. The determination is repeated to confirm the accuracy of the result. The next step is to determine the F.P. depression constant using some substance such as naphthalene ( $C_{10}H_8$ , M.W.128). A clean specimen tube is weighed, about 0.2 gram of naphthalene put in and the tube reweighed: then about 2 grams of finely divided camphor is added and the tube and its contents again weighed. A loosely fitting cork is put in the tube which is heated over a small flame so as to melt the contents at as low a temperature as possible. While cooling, the contents are swirled round to keep the mixture homogeneous. The solid contents of the tube are removed with a spatula, or if necessary the tube is broken and the contents are ground up in a mortar: the material so obtained is then used for a melting point determination carried out in exactly the same manner as that for the camphor alone. With the mixture before the melting-point is reached an appearance is seen first like that of melting ice and then of a turbid liquid. If this is carefully examined with a lens, a sharp crystalline skeleton can be distinguished, which at first permeates the whole mass and which, on slowly heating, disappears from the top downwards. The disappearance of the last trace of crystals from the bottom is to be taken as the melting-point of the mixture. From these results the F.P. depression constant is calculated. Finally the experiment is repeated in each detail as for the naphthalene, but using the substance for which the molecular weight is required. With an unknown substance a fresh determination would be made using a new mixture containing a higher percentage of camphor to make sure that the whole of the solute was in solution. The camphor method has been modified by Reilly and Pyne<sup>1</sup> so as to enable small depressions to be estimated with accuracy, and so permit of the determination of molecular weights from quite small depressions of freezing-point.

Though devised to meet a particular difficulty presented by the pigment produced by *Chromo-bacterium violaceum*, it is of general application, and it will be described here in detail.

The method briefly depends on the preparation of cooling curves for slowly cooling camphor before and after the addition of the substance whose molecular weight is to be determined. As only small amounts of camphor

<sup>1</sup> *Sci. Proc. Roy. Dub. Soc.*, 1927, 18, 42, 489.

are employed, the thermometer should be small-bulbed. An Anschütz thermometer, graduated in fifths of a degree, and capable of being read by means of a mounted lens to one-fiftieth of a degree Centigrade, is quite suitable. The procedure is as follows:

0.3–0.7 gram camphor (Kahlbaum's, further purified by sublimation) is introduced into a small, fairly strong test-tube (10 mm.  $\times$  60 mm.), which is closed by a well-fitting cork, carrying the thermometer. The tube is then immersed up to 2–3 mm. from the bottom of the cork in glycerine

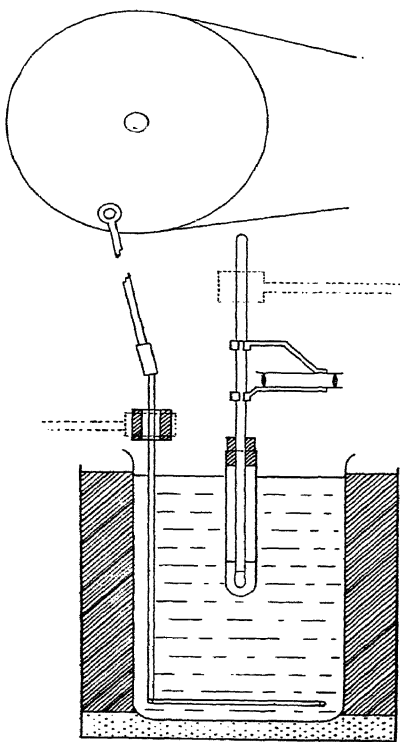


FIG. 31 (XIII)

contained in a 400-ml. beaker, which forms the heating bath. It is necessary to close completely the test-tube in this manner, and almost totally immerse it in the bath, in order to prevent sublimation of the heated camphor. The heating beaker is contained in a second vessel (an ordinary tin container serves well), the bottom of which is covered with a layer of sand; and the annular space between the two is filled with loose asbestos. The object of this insulation is to enable cooling to take place sufficiently slowly to give a cooling curve with a well-defined melting-point flattening. A motor-driven stirrer is used, to prevent inequalities of temperature in the glycerine, and thus ensure a perfectly uniform rate of cooling. When the test-tube containing the camphor is in position, the bath is heated to about  $180^\circ$  by a Meker burner. As soon as the camphor melts, the thermometer is lowered or adjusted through the cork, so that its bulb is completely covered by the camphor, and centrally positioned. The Meker is then replaced by an ordinary Bunsen or Argand burner, turned down fairly low—the size of the flame being so adjusted that the rate of cooling of the camphor does not

exceed  $0.8^\circ$  per minute. A rate of  $0.4^\circ$ – $0.8^\circ$  per minute is the most favourable. The motor stirrer is then set going, and, after the temperature has fallen to  $178^\circ$ , it is read every quarter of a minute by means of an eyepiece mounted on the thermometer. (See Fig. 31 (XIII).) It is unnecessary to plot the readings to determine the melting-point. The temperature is always found to remain steady for two or three readings at some point, which is taken to be the melting-point. Sometimes a slight rise in temperature occurs, and then the highest point reached is taken. It is advisable, however, to take readings every quarter of a minute, and not to depend on observation

alone to determine the point at which the temperature remains steady, for the latent heat of the small amount of camphor used only produces a very momentary effect on the rate of cooling, which might easily be missed.

While the camphor is still hot, or after it has been remelted if necessary, the thermometer is taken out, allowed to cool, and any camphor which has sublimed around the cork is removed. 2–5 mg. of the substance whose molecular weight is required are compressed to form a small pellet (or a single crystal may be used), weighed on the micro-balance, and dropped into the tube. The stopper and the thermometer are inserted once more, and the tube heated up again in the glycerine bath. As soon as the camphor melts, the test-tube is gently shaken to ensure proper solution of the added substance, the thermometer properly adjusted in the melt, and the cooling curve determined as before. After the estimation, the cork and thermometer are taken out, and the tube is freed from camphor which has sublimed near the cork, and then weighed. The weight of camphor in which the substance was dissolved at the moment of the estimation can thus be determined.

The following are examples of some molecular weight determinations made in this manner by Reilly and Pyne<sup>1</sup>:

$\Delta$  = Depression of freezing-point.

M. = Molecular weight.

Mol. coeff. of lowering (for camphor) =  $40^\circ$  (1 gram mol. in 1 kg.).

1. Acetanilide, 2.54 mg. in 432 mg. camphor.

$\Delta = 1.80^\circ$

Found M. = 129. Theor. M. = 135.

2. Strychnine, 5.11 mg. in 524 mg. camphor.

$\Delta = 1.18^\circ$ .

Found M. = 331. Theor. M. = 334.

3. Palmitic Acid, 5.23 mg. in 689 mg. camphor.

$\Delta = 1.18^\circ$ .

Found M. = 257. Theor. M. = 256.

4. *o*-Benzoyl di-*p*-tolyl oxide 3.814 mg. in 293 mg. camphor.

$\Delta = 1.66^\circ$ .

Found M. = 314. Theor M. = 302.

The apparatus described is constructed from the simplest materials. Its use, of course, involves that of a micro-balance, since it is a micro-method. No doubt it could be made still more sensitive, and therefore available for use with even smaller amounts of substances, or those which are less soluble, by some further slight changes. By employing, e.g. a small bulb thermometer graduated in one-tenths of a degree, and a short-focus table cathetometer for reading the temperature, its sensitiveness could easily be increased four-fold; the use of a thermo-couple would increase the sensitiveness still more. Electrical heating might also be used, and would give both a quicker heating up and a more easily controlled cooling than gas.

The most important manipulative matter is the proper adjustment of the rate of cooling. If this is too rapid, the latent heat evolved on the

<sup>1</sup> *Sci. Proc. Roy. Dub. Soc.*, 1927, 18, 42, 489.



solidification of the camphor is insufficient to counterbalance it, and a steady fall of temperature ensues, in which no point of arrest can be detected.

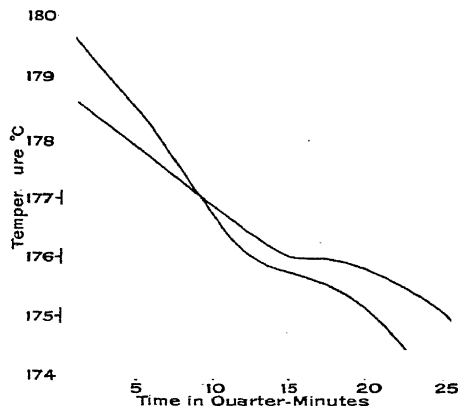


FIG. 32 (XIII)

from the walls of the tube. Neglect of this precaution leads to the production of a cooling curve of type 1, in which no clearly defined melting-point is discernible.

Dupont<sup>1</sup> states that camphenylone obtained by the oxidation of camphene by nitrogen peroxide is a good cryoscopic solvent. The melting-point is about 35° and the constant 600.

<sup>1</sup> *Bull. Soc. Chim.*, 1933, 1159.

A rate of fall of about 0.8°, or less, per minute has been found to give satisfactory results. Fig. 32 (XIII) shows two cooling curves which illustrate this fact. In one curve the rate of cooling was about 1.6° per minute; in the other 0.85° per minute. The second curve shows a marked flattening at one section which denotes the freezing-point of the camphor, while the first shows a continuous fall of temperature without any break. Besides ensuring that the rate of cooling is low enough, the only other point which needs attention is the very obvious, but important, one of inserting the thermometer so that the bulb is completely surrounded by camphor, and equidistant

## SECTION 4: PARTITION COEFFICIENTS

**The Law of van't Hoff <sup>1</sup> or Henry.** This law states that if a substance has the same molecular weight in the gaseous and dissolved states, its partial pressure in the vapour is proportional to the concentration in the solution. It can be shown that if the vapour is in equilibrium with separate solvents the ratio of the concentrations of the two solvents will be constant. If the two solvents are immiscible then we have a constant ratio of concentration in the two solvents as long as the molecular weight of the solute is the same in both. This is the partition law. When the concentrations in the two solvents have their maximum values each of the solutions is saturated and we have

$$\frac{C_a}{C_b} = r = \frac{S_a}{S_b}$$

where  $C_a$  and  $C_b$  are the concentrations of the solute in the solvents  $a$  and  $b$ ,  $r$  is the constant ratio, and  $S_a$  and  $S_b$  are the solubilities of the solute in the solvents  $a$  and  $b$ . This equality has been proved by Jakowkin, for the distribution of iodine between water and carbon tetrachloride and a number of other solvents. When the solvents are not completely immiscible, as in the case of ether and water, the relationship will not hold so exactly because  $S_a$  and  $S_b$  will now represent the solubilities of the solute in  $a$  saturated with  $b$  and in  $b$  saturated with  $a$ , and at other dilutions the amount, for example, of  $b$  required to saturate  $a$  will be modified by the presence of the solute.

**Wider Application of Law.** Nernst has extended the principle to those cases where chemical reaction takes place between the different molecular species. For example, if a substance undergoes partial electrolytic dissociation in one solvent but not in the other we get a constant ratio between the concentrations of the still undissociated molecules in the two solvents; thus succinic acid is slightly dissociated in water but not in ether, and we get a constant ratio between the total concentration in the ether and the concentration of the undissociated fraction of the acid in the water.

**Example of the Determination of the Partition Coefficient.** As an example of the use of a substance which has a normal molecular weight in both solvents, the partition of iodine between water and carbon tetrachloride studied by Jakowkin will be taken. At 25° the solubilities are 0.3395 gram in 1 litre of water and 30.33 in 1 litre of saturated carbon tetrachloride, i.e. saturated solutions are roughly N/400 and N/4; therefore 200 ml. of the former would require 25 ml. of N/50 thiosulphate, while 10 of the latter would require 25 ml. N/10 thiosulphate.

Taking three 500-ml. bottles with glass stoppers, we place 100 ml. of carbon tetrachloride and 300 ml. of water in each and 3, 2, and 1 grams of

<sup>1</sup> So called by Nernst.

iodine respectively. The stoppers are put in and rubber caps secured over the stoppers and necks and the bottles are shaken in the thermostat for 2 hours. At the end of that time they are removed from the shaker and fixed vertically for the two layers to separate; with the present solutions this occurs quickly, but some solutions take hours to clear up.

10 ml. of the lower carbon tetrachloride solution are then removed with a pipette, avoiding inclusion of any of the upper layer. This can be done by placing the moistened forefinger of one hand over the end of the pipette and grasping the bulb with the other hand just before putting the point in the solution. The warmth of the hand expands the air in the pipette so that small bubbles escape while it passes through the upper layer. 10 ml. are then sucked up, the pipette removed, the outside wiped, and the solution is titrated with N/10 thiosulphate after the addition of water. The bottles are re-stoppered, shaken again for an hour, and another 10 ml. are withdrawn and titrated, and so on until constant results are obtained; 200 ml. of the top layer are then titrated with N/50 thiosulphate. Jakowkin obtained such results as the following:

Grams of iodine per litre of CCl <sub>4</sub> solution	Grams of iodine per litre of water solution	$\frac{C_1}{C_2}$
8.5	0.10	85.0
17.5	0.20	87.5
30.3	0.34	89.2

*The Distribution of an Acid between Two Solvents in one of which it Dissociates.* Chandler's experiments with succinic acid between ether and water may be taken as an example. Succinic acid is purified by recrystallization from distilled water. The ether is shaken with dilute sodium hydroxide solution, washed repeatedly with distilled water and then distilled; the middle portion of the distillate is used or Werner's method of shaking with silver hydroxide may be used. A stock solution of succinic acid containing 20 grams per litre is made up and is diluted as required; e.g. dilutions of 1.5, 10, 25, and 100 might be used. Equal volumes, say 200 ml., of the ether and the aqueous acid solution are shaken together in the thermostat in the usual way, allowed to stand for half an hour, and then a sample of the aqueous solution is removed for analysis, the glass pipette bulb being warmed by the hand and its tip passed through the ether layer. The process is repeated until a constant value is obtained, when a sample of the ether layer is also analysed. N/10 barium hydroxide is used for the more concentrated solutions and N/50 for the more dilute; the indicator is phenolphthalein. Before titrating the ethereal solution, water is added and the ether is distilled off.

**Method of Calculation.** Let  $k_1$  be the primary ionization constant of the acid.

Let  $A$  be the molecular concentration of the aqueous layer

$\alpha$  be the degree of ionization of the aqueous solution

$p$  be the ratio total concentration of the acid in aqueous solution to concentration of acid in the ether solution

$P$  be the true partition coefficient; e.g. the ratio of the concentration of the undissociated acid in the aqueous layer to the concentration of the acid in the ether layer

Then  $\alpha$  can be calculated from the dilution law,  $(1 - \alpha)V = k_1$  and  $P$  from the relation  $P = p(1 - \alpha)$ .

Some results obtained by Chandler for succinic acid at 25° were :

$$k_1 = 66.5 \times 10^{-6}$$

A	100 $\alpha$	$\frac{p}{P}$	$\frac{P}{P_0}$
0.1708	1.9	7.73	7.59
0.0287	4.7	7.73	7.36
0.0120	7.2	7.95	7.37
0.0039	12.2	8.42	7.39
0.0023	15.6	8.79	7.42

**Further Example.** Nernst's principle can also be applied to the case when the substance is associated in one of the solvents and dissociated in the other. Dawson's results for the distribution of acetic acid between water and chloroform illustrate the case. Here the acid is associated in the chloroform and dissociated in the water. The strongest aqueous solution of acetic acid used was approximately 1.8 normal, other solutions being prepared by diluting this down to ten times; 60 ml. of the solution and 60 ml. of the chloroform were placed in a cylindrical separating funnel and immersed in a thermostat, with the exit end projecting to keep it dry. At intervals of 5 minutes for a period of 0.75 hour the funnel was removed and violently shaken by hand. The two phases were allowed to separate in the thermostat for 0.5 hour, and the two layers were then run off into separate stoppered tubes for analysis. N/4 and N/40 solutions of caustic soda free from carbonate were used for the titrations.

**Method of Calculation.** Let  $C_1$  and  $C_2$  represent the total acid concentrations in the water and chloroform respectively.

Let  $\alpha$  be the dissociation fraction in the water solution.

Then  $C_1(1 - \alpha)$  is the concentration of undissociated acid in the water.

If  $r$  is the distribution ratio for simple molecules of the acid between water and chloroform,  $\frac{C_1(1 - \alpha)}{r}$  is the concentration of the simple molecules of acid in the chloroform and  $C_2 - \frac{C_1(1 - \alpha)}{r}$  that of the double molecules. Then from the Law of Mass Action :

$$\frac{\left\{ \frac{C_1(1 - \alpha)}{r} \right\}^2}{C_2 - \frac{C_1(1 - \alpha)}{r}} = K_1 = \frac{C_1^2(1 - \alpha)^2}{r^2 C_2 - r C_1(1 - \alpha)}$$

The dissociation constant  $K$  for acetic acid at 25° is  $1.8 \times 10^{-5}$ , hence the values of  $\alpha$  can be calculated for each dilution from Ostwald's dilution formula  $\frac{\alpha^2}{(1 - \alpha)V} = K$ . From any pair of experimental results we can now calculate a value for  $r$ : using the second and fifth experiments shown below, the value of  $r$  is found to be 42.9, and having obtained this we can get  $K_1$ . A few of Dawson's figures will illustrate the results obtained :

$C_1$	$C_2$	$C_1(1 - a)$	$\frac{C_1(1 - a)}{r}$	$C_2 - \frac{C_1(1 - a)}{r}$	$K_1$
1.535 . .	0.2277 .	1.530 .	0.03565 .	0.1920 .	0.0066
0.9084 . .	0.08904 .	0.9048 .	0.02109 .	0.06795 .	0.0065
0.6089 . .	0.04557 .	0.6052 .	0.01411 .	0.03146 .	0.0063
0.2696 . .	0.01222 .	0.2675 .	0.006234 .	0.005986 .	0.0065
0.1946 . .	0.007586 .	0.1929 .	0.004495 .	0.003091 .	0.0065

The calculations are based on the assumption that the addition of acetic acid does not alter the miscibility of the chloroform and water; in fact, their mutual solubility is increased by acetic acid, so that the constancy of the values of  $K_1$  shown in the last column is of fictitious value. Bancroft points out that the agreement of results with a formula does not always prove that the premises on which the formula is based are correct.

**Freezing-point Method.** Nernst investigated a similar case, the distribution of acetic acid between benzene and water, by means of the freezing-point. In one experiment, using the Beckmann freezing-point apparatus, 5.075 grams of water and 31.5 grams of benzene were placed in the tube. The freezing-point was found to be  $5.9^\circ$  (only the benzene layer freezing), and this, owing to the very slight solubility of water in benzene, is practically the freezing-point of pure benzene. Small weighed quantities of acetic acid were then added. The acid distributed itself between the two solvents, and when the freezing-point (that of the benzene solution) was determined, this was lowered by the acetic acid dissolved in it. To find the concentration corresponding to a given lowering of the freezing-point of the benzene solution, a separate series of experiments was carried out in which weighed quantities of acetic acid were added to a weighed amount of benzene, no water being present. From the curve so obtained the concentration of the acid in benzene corresponding to a given lowering could be determined; then, knowing the total amount of acid and benzene present, the amount of acid in the water layer can be obtained.

**Results.** Calling  $C_1$  the number of grams of acetic acid in 5.07 grams of water, and  $C_2$  the number of grams of acetic acid in 31.5 grams of benzene, the following results were obtained:

$t^\circ \text{C.}$	$C_2$	$C_1$	$\frac{C_1}{C_2}$	$\frac{C_1^2}{C_2}$
0.075 . .	0.043 . .	0.245 . .	5.7 . .	1.40
0.120 . .	0.071 . .	0.314 . .	4.4 . .	1.39
0.158 . .	0.094 . .	0.375 . .	4.0 . .	1.49
0.240 . .	0.149 . .	0.500 . .	3.4 . .	1.67

**Distribution of a Base between Two Acids.** Dawson and Grant used the partition method to determine the ratio of the distribution of a base between two acids. If the solution contains the two acids HA and HB and the base MOH, neglecting dissociation we shall have present the four substances HA, HB, MA, MB, if there is insufficient base to neutralize both the acids. If now the solution is shaken up with an immiscible solvent capable of taking up only one of these four substances, say HA, we can determine the proportions of the four substances if we know the amounts of acids, and the base used. It was found that while acetic acid was used, the distribution of caustic soda between acetic acid and

tartaric acid. The first step was to determine the distribution of acetic acid between chloroform and water: the method used has been described in the previous section. A diagram was then plotted showing the relation between the concentration of the chloroform,  $C_2$ , and the ratio  $C_1/C_2$ . From this curve, the value of  $C_1$ , corresponding to an experimental value of  $C_2$ , can be worked out. The influence of sodium acetate and tartaric acid on the distribution of the acetic acid between the water and chloroform was tested experimentally and found to be so small as to be negligible. Normal solutions of acetic acid, tartaric acid, and caustic soda were then prepared. Equal quantities of the three solutions were mixed, using a small excess of acetic acid to compensate for that taken up by the chloroform, and the mixture diluted to the required volume; for example, in one experiment 20 ml. of N tartaric acid, 20 ml. of N sodium hydroxide, and 20.7 ml. of N acetic acid were mixed and diluted to 100 ml. 60 ml. of this solution were shaken with 60 ml. of chloroform. On titration the aqueous layer was found to contain 0.1990 gram equivalents per litre of acid and the chloroform layer 0.005632.

The original N tartaric acid was diluted to 0.2N in making up the mixture.

The original N sodium hydroxide solution was diluted to 0.2N in making up the mixture.

The acetic acid therefore from the titration is 0.199N.

From the curve the distribution ratio when the chloroform solution contains 0.005632 is found to be 28.3, hence the free acetic acid in the aqueous solution is  $0.005632 \times 28.3 = 0.1593$ . The sodium acetate must then be  $0.199 - 0.1593 = 0.0397$ . This leaves  $0.2 - 0.0397$  of 'caustic soda' to combine with tartaric acid, hence the sodium tartrate is 0.1603 gram equivalents per litre and so the uncombined tartaric acid will be  $0.2 - 0.1603 = 0.0397$ . The ratio of sodium tartrate to sodium acetate is therefore

$$\frac{0.1603}{0.0397} = 4.04$$

**The Hydrolysis of Salts.** Such a measurement has also been made by means of distribution experiments by Farmer. Suppose a gram molecule of aniline hydrochloride is dissolved in  $V$  litres of water. If the degree of hydrolysis is  $x$ , the concentration of free aniline and free hydrochloric acid will be  $x/V$  gram molecules per litre. If the distribution ratio of aniline between benzene and water is first determined and then the aniline hydrochloride solution is shaken with benzene and the aniline concentration in the latter is determined, from the distribution ratio of the concentration of the free aniline the amount of water is obtainable, and then, knowing the amount of aniline hydrochloride originally present, the degree of hydrolysis can be calculated. In one experiment 1 litre of water, containing 0.09969 gram molecule of aniline hydrochloride, was shaken with 60 ml. of benzene at 25°. The benzene layer was found to contain 0.001156 gram of aniline per ml.;

59 ml. of benzene therefore contained  $\frac{59 \times 0.001156}{93}$  gram molecules of

aniline = 0.000733; 59 ml. is used in the calculation instead of 60 ml., to allow for the solubility of benzene in water. The water therefore contains  $0.09969 - 0.000733 = 0.098957$  gram molecule of free and combined aniline.

The partition coefficient being 10.1 (benzene/water) the molecular concentration of free aniline in the water layer is  $\frac{1.156}{93 \times 10.1} = 0.001232$ , and the amount of combined aniline must therefore be  $0.098957 - 0.001232 = 0.097725$  gram molecule. This will also be the amount of combined acid, leaving  $0.09969 - 0.09773 = 0.00196$  of free acid.

$x$  being the fraction hydrolysed, we have :

$$\frac{x^2}{(1-x)V_m} = \text{const.} = \frac{0.00123 \times 0.00196}{0.09773} = 0.0000247$$

whence  $x = 0.0156$  or 1.56 per cent.

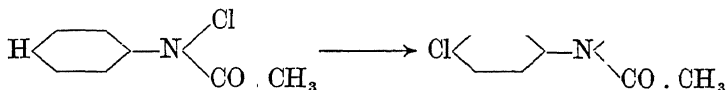
The first step in the experiment is to determine the distribution of aniline between benzene and water: 1,000 ml. of water and 60 ml. of benzene are used; 1 ml. of benzene is found to go into solution in the water, leaving 59 ml.; 0.2 gram of aniline is then added and the mixture shaken in the thermostat until equilibrium is attained; 50 ml. of the benzene layer after filtration are removed and the aniline hydrochloride is precipitated by means of a current of dry HCl gas, the benzene evaporated off and the aniline hydrochloride weighed. The experiment is then repeated, using 0.1 gram of aniline. The total weight of aniline used is known, the weight in the benzene layer can be calculated, and so by difference that in the water layer.

**Further Applications.** Other practical applications of the distribution law are Dawson and McRae's work on metal ammonium compounds by the distribution of ammonia between aqueous solution and chloroform; the extraction of alkaloids by shaking aqueous solutions with chloroform, e.g. Siedell found that 0.125 gram of strychnine shaken with a mixture of equal volumes of water and chloroform distributed itself in the ratio of 0.002 to 0.123, so that the alkaloid in an aqueous solution can be removed practically completely by shaking three times with an equal volume of chloroform. Another example is the determination of the higher alcohols in spirits. The distillate containing ethyl alcohol and the higher alcohols is brought to a specific gravity of 1.1 by the addition of a saturated sodium chloride solution and is then shaken successively with 40, 30, 20, and 10 ml. of carbon tetrachloride, in which the higher alcohols are soluble but not the lower.

## SECTION 5: RATES OF REACTION

**Law of Mass Action.** Guldberg and Waage stated the law of mass action, namely, that the rate at which a substance reacts is proportional to the active mass of that substance and also that when chemical equilibrium is established it is due to opposing reaction velocities neutralizing each other. By active mass, molecular concentration is meant. Individual cases of the application of the law had been studied at an earlier date, notably the case of the inversion of cane-sugar by Wilhelmy in 1850, in which he correctly applied the law of mass action and first used the differential equation to get the velocity constant.

*Examples.* The simplest possible case is that in which one molecular species only undergoes change. An example of such a change is the conversion of acetochloranilide into the isomeric *p*-chloro-acetanilide.



Calling these substances A and B, if we start with a concentration of  $a$  gram molecules of A per litre, according to Guldberg and Waage's law the rate at which A will be transformed into B will be proportional to  $a$ , it will therefore be equal to  $Ka$  where  $K$  is a constant called the velocity constant of the reaction. After a time  $t$  a certain quantity  $x$  of A will have been transformed into B so that the concentration of A is reduced to  $a - x$ ; at this instant, then, the rate of the reaction is proportional to  $a - x$  and is equal to  $K(a - x)$ , where  $K$  has the same value as before. We can therefore write

$$\frac{dx}{dt} = K(a - x)$$

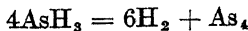
On integration this gives

$$K = \frac{1}{t} \log_e \frac{a}{a - x} \\ = \frac{2.302}{t} \log_{10} \frac{a}{a - x}$$

Since the instant at which the reaction starts may not be known with certainty, it is often useful to write the equation in the form

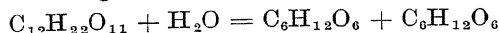
$$K = \frac{2.302}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$$

where  $x_1$  and  $x_2$  are the amounts of A converted in the times  $t_1$  or  $t_2$ . Reactions of this kind are called monomolecular. Some examples are the decomposition of arsine and phosphine, e.g.

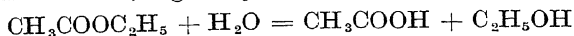




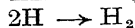
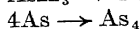
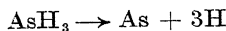
the inversion of cane-sugar into glucose and fructose,



the hydrolysis of esters, e.g. ethyl acetate



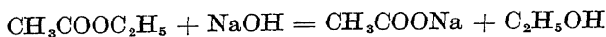
**Monomolecular Reaction.** In the first example it appears at first sight that 4 molecules are involved in the change, yet it obeys the monomolecular law. This is supposed to be due to the reaction taking place in the stages



The last two reactions are extremely rapid, the first is comparatively slow, so that for all practical purposes the time of the first stage is the time of the whole reaction. In the second and third cases 2 molecules appear to be involved. Here the reaction obeys the monomolecular law because in the concentration employed the active mass of the water remains practically constant. For example, if we take a 10 per cent solution of cane-sugar, we have 10 grams of sugar to 90 grams of water, the molecular weight of the sugar is 342, while that of the water is 18. The relative molecular concentrations are then  $\frac{10}{342}$  to  $\frac{90}{18}$ , i.e. as 1 : 171. Thus, when the sugar undergoes

100 per cent change, the water undergoes a change of about 0.6 per cent.

**Bimolecular Reaction.** When 2 molecules are actually involved in the change so that the active masses of both are altered, we get a true bimolecular reaction. The saponification of ethyl acetate by means of sodium hydroxide illustrates this case :



Suppose the initial molecular concentration of the ester to be  $a$  gram molecules per litre and of alkali to be  $b$ . After a time  $t$  let  $x$  molecules of ester have undergone change ; the change of  $x$  molecules of ester involves the change of the same number of molecules of the alkali. At the time  $t$  the molecular concentrations of ester and alkali are  $a - x$  and  $b - x$  respectively. The rate of reaction is then

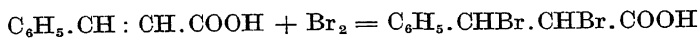
$$\frac{dx}{dt} = K(a - x)(b - x)$$

This on integration gives

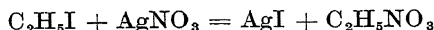
$$K = \frac{(a - b)t}{(a - x)(b - x)} \log_e \frac{(a - x)b}{(b - x)a}$$

Other examples of second-order reactions are :

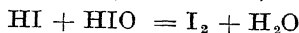
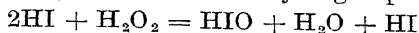
(1) The bromination of cinnamic acid—



(2) The action of silver nitrate on ethyl iodide in alcoholic solution—

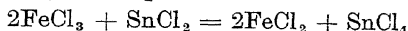


(3) The action of hydriodic acid on hydrogen peroxide—



—the former reaction being the slower of the two.

**Trimolecular Reaction.** By reason of the fact that many complex reactions take place in stages, reactions of a higher order than the second are uncommon. An example of a trimolecular reaction is that studied by Noyes and expressed by the equation



Here it was found desirable to add a small amount of the products of the reaction to prevent secondary disturbances. When the three substances are present initially in the same molecular concentration

$$\frac{dx}{dt} = K(a - x)^3$$

and

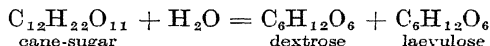
$$K = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2}$$

Reactions of the fourth and fifth order have been found, but are extremely rare.

Each individual case must be treated according to circumstances, and it is possible therefore to give only a selection of examples to illustrate the way in which the measurements are made.

## MONOMOLECULAR REACTIONS

### (1) The Inversion of Cane-sugar :



Cane-sugar is dextrorotatory, that is, it rotates the plane of polarization to the right. Dextrose is also dextrorotatory ( $[\alpha]_{20}^D = +52.5^\circ$ ), but laevulose is more strongly laevorotatory ( $[\alpha]_{20}^D = -92^\circ$ ), so that a mixture of equal quantities of the two reaction products is as a whole laevorotatory. As the change proceeds, therefore, the amount of dextrorotation gradually decreases to zero, and the solution then become laevorotatory. The progress of the change can thus be followed by means of the polarimeter. The reaction takes place slowly, but is accelerated by acids, so that in order to complete the experiment within a reasonable time an acid solution is used. 20 grams of pure cane-sugar are dissolved in a 100-ml. flask, a crystal of mercuric iodide is added as a preservative, and the solution is made up to the mark with distilled water. A normal solution of hydrochloric acid is also prepared. When equal quantities of these two are mixed we have a 10 per cent cane-sugar solution in N/2 hydrochloric acid; the solutions are to be mixed immediately before the first reading is taken. Two flasks which have been steamed and dried in the usual manner are taken, and into one 25 ml. of sugar solution, and into the other 25 ml. of the HCl solution, are placed. The stoppers are inserted and the flasks are placed in the thermostat at the required temperature, say  $25^\circ$ . A jacketed polarimeter

tube is then taken and filled with water, the water circulation from the thermostat is started, and the constancy of temperature of the water in the tube is determined. The water circulation must be regulated so that the temperature is constant to  $0.1^\circ$ , since velocity constants are very sensitive to temperature; in this particular case it becomes 3.63 times as great for a rise of  $10^\circ$ . The zero reading of the polarimeter can now be made, taking the mean of a number of settings. The tube is next removed and dried, replaced in the polarimeter and allowed to remain there for ten minutes. The two flasks are then removed from the thermostat, their contents are mixed by passing backwards and forwards from one to the other, and the mixture is placed in the polarimeter tube. The initial readings must then be taken as rapidly as possible. The time is taken, five settings of the polarimeter are made and recorded, and the time again noted. The mean of the five readings is taken as the initial rotation and the mean of the two times is the initial time.

After 10 minutes a similar series of five readings of the polarimeter and of the mean time is taken. Similar series are then taken over periods gradually increasing up to 2 hours. The reaction will not be complete until at least 48 hours have elapsed, when a final series of readings must be made. The zero-point of the instrument is then once more determined to ensure that no change has occurred therein.

If the initial and final readings are denoted by  $a_0$  and  $a_\infty$  and the reading at time  $t$  is  $a_t$  the amount which has changed in the time  $t$  is  $a_0 - a_t$ , and the amount still left unchanged is  $a_t - a_\infty$ . The total amount of sugar present is proportional to  $a_0 - a_\infty$ , so that

$$\begin{aligned} K &= \frac{1}{t} \log_e \frac{a_0 - a_\infty}{a_t - a_\infty} \\ &= \frac{2.302}{t} \log \frac{a_0 - a_\infty}{a_t - a_\infty} \end{aligned}$$

Some results of Wilhelmy, using nitric acid as the catalyst at  $15^\circ$ , show the results attainable :

$t$ , minutes	$a_t - a_\infty$	$\log_{10} \frac{a_0 - a_\infty}{a_t - a_\infty}$	$K$
0 . . .	65.45	—	—
45 . . .	56.95	0.0605	0.00134
90 . . .	47.45	0.1217	0.00135
150 . . .	40.70	0.1981	0.00132
210 . . .	33.70	0.2380	0.00137
270 . . .	26.95	0.3851	0.00142

*Strength of Acids.* The same reaction can be used to determine the relative strengths of acids, since these are proportional to their catalysing powers. All that is necessary is to carry out the experiment as described above, but using different acids, each in N/2 solution in the final mixture used. The ratio of the various velocity constants obtained is then the ratio of the strengths of the acids used as catalysts.

(2) **The Decomposition of Arsine :**



Arsine is extremely poisonous, and the following is intended only as a description of a method; it is not to be used as a student's experiment. The apparatus is that shown in Fig. 33 (XIII). The reaction vessel A is enclosed in the heating reservoir B, where it is heated to a constant temperature by means of diphenylamine (310°) boiling under the reflux condenser G. The tap D is closed and A is connected to the pump and evacuated; the arsine is then introduced and the tube E is sealed. A is placed in a vessel containing water at the room temperature, the tap D is opened and by raising or lowering the reservoir the mercury is brought to a marked point in C. The height of the barometer and the heights of the mercury in C and F are read, so that the pressure of the gas in A is known. We then have the pressure of the gas at a known volume and temperature. When decomposition occurs the pressure rises at a fixed volume and temperature in the ratio of 2 to 3 (the volume of the solid As is neglected). Hence, if the initial pressure were  $P_0$ , when the reaction

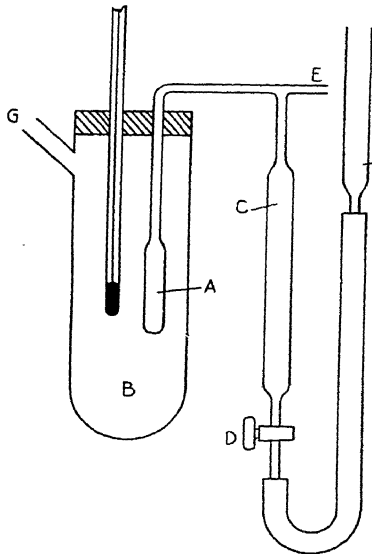


FIG. 33 (XIII)

is complete the pressure will be  $\frac{3P_0}{2}$  and at the time  $t$  it will be  $P_t$ , hence the change in pressure corresponding to the completed reaction is  $\frac{3P_0}{2} - P_0 = \frac{P_0}{2}$ . When the pressure is  $P_t$  the change in pressure which has yet to be completed is  $\frac{3P_0}{2} - P_t$ , and this is of course the arsine as yet unchanged.

Hence

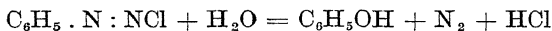
$$\frac{dx}{dt} = K \left( \frac{3P_0}{2} - P_t \right)$$

$$K = \frac{1}{t} \log_e \frac{\frac{P_0}{2}}{\frac{3P_0}{2} - P_t} = \frac{1}{t} \log_e \frac{P_0}{3P_0 - 2P_t}$$

Therefore after the initial readings have been made A is dried and placed in the diphenylamine vapour for 2 or 3 hours; it is then removed, cooled, and the new pressure read for the same volume. Proceeding in this way the following results were obtained at 310°:

Time in hours	Pressure in mm. of Hg	K
0 .	784.84 . . .	—
3 .	878.5 . . .	0.0908
4 .	904.05 . . .	0.0905
5 .	928.02 . . .	0.0908
	949.28 . . .	0.0905
	969.08 . . .	0.0906
	987.19 . . .	0.0906

### (3) The Decomposition of Benzene Diazonium Chloride and other Diazonium Salts :



From the equation it is seen that the volume of the nitrogen set free is proportional to the amount of chloride decomposed. The reaction is carried out in dilute aqueous solution, and it is found that such a solution readily remains super-saturated with nitrogen ; it is therefore necessary to stir the reaction mixture throughout the progress of the reaction. This can be done by means of a stirrer working through a mercury seal as shown in Fig. 34 (XIII). S, the stem of the stirrer, passes through the tube *a*, 4 cm. long, which passes through the rubber stopper *e* ; *b* is a tube 3 cm. long and

12 mm. external diameter, which passes half-way through the stopper *e*. Mercury is poured between *a* and *b*. On the stem S is fixed by means of rubber tubing a short piece of tube *c*, which bears on the top of *a*, and on *c* is fixed by means of a rubber stopper the tube *d*, which is intermediate in diameter between *a* and *b*, and which dips down into the mercury. A coat of vaseline on S serves to diminish friction. The reaction is carried out in a large test-tube (15 cm. by 3 cm.) which has a narrow-bore side-tube at the top for connecting to a Hempel burette. Since the experiment continues for a considerable time the measuring tube of the burette should be surrounded by a water jacket so that its temperature can be kept constant. The solutions must be freshly prepared for each experiment ; 6.64 grams of pure aniline are dissolved in 21.5 ml. of hydrochloric acid (specific gravity 1.16), 4.93 grams of sodium nitrite are dissolved in 75 ml. of water. The two solutions are cooled in ice and the nitrite is then slowly added to the aniline solution by

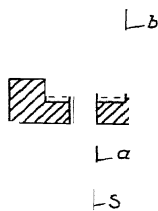


FIG. 34 (XIII)

means of a dropping funnel, the lower end of which dips below the surface of the aniline solution. The mixture is kept well shaken, and the rate of addition controlled so that the temperature is kept low. The solution so obtained is then made up to 1 litre, giving a solution containing 10 grams of the diazonium chloride per litre. Sufficient of the solution is placed in the test-tube to fill it nearly to the level of the side-tube. The stopper and stirrer are inserted and the tube is fixed in the thermostat (25°) and the stirrer is started. After 7 to 10 minutes the side-tube is joined to the burette and this time is taken as the zero time for the experiment. The burette is levelled to atmospheric pressure, the volume and temperature

readings are taken and recorded, and also the height of the barometer. The next reading is taken after 2 hours and then at intervals of an hour, the pressure in the burette being adjusted to atmospheric each time, and volume, temperature, and barometric height being recorded. After 8 hours the reaction may be brought to completion so as to obtain the total volume of nitrogen. This is done by removing the tube from the thermostat and placing it in a beaker of hot water for 15 minutes, replacing in the thermostat, and after 10 minutes reading the volume. This process is repeated until the volume remains unaltered, indicating the completion of the reaction. The velocity constant can then be calculated from the volume of nitrogen set free.

Typical results from diazotizing aniline in hydrochloric acid are as follows [61 ml. is the total volume of nitrogen (at 14° and 741 mm.) calculated from the amount of aniline used]:

Time in minutes Solution kept at 20°	Volume of nitrogen in ml. at 14° and 741 mm.	K
451 . . . . .	31.4 . . . . .	0.00159
506 . . . . .	34.4 . . . . .	0.00163
607 . . . . .	40.5 . . . . .	0.00179
1382 . . . . .	55.3 . . . . .	0.00170
∞ . . . . .	61.0 . . . . .	—

The diazonium salts from heterocyclic amines generally show a close resemblance to similar substances from aromatic amines. Many of the heterocyclic diazonium salts, however, even in ring compounds of a simple nature, show a remarkable stability, in marked contrast with corresponding benzenoid substances.

The titration method of Hirsch is generally not satisfactory for the investigation of these substances. The direct application of the physico-chemical method of Hausser and Müller is also to some extent unsatisfactory. A more recent process for the study of the decomposition of diazonium salts consists in heating, in a thermostat, a solution of the diazonium salt contained in a quartz tube, through which a current of air-free carbon dioxide (prepared by Farmer's method<sup>1</sup>) is passing, and collecting the nitrogen evolved over potassium hydroxide solution. The apparatus used by Reilly and Madden<sup>2</sup> is shown in Fig. 35 (XIII). A definite volume of a solution containing a known weight of the amine (sufficient to give 56 ml. of gas at *S.T.P.*, normal diazotization being assumed) was heated in a specially constructed quartz vessel, A, fitted with a ground stopper into which was sealed a tube passing to the bottom of the vessel. The vessel was contained in a thermostat, B, at 101.5°, which temperature was found to keep the solution of the diazonium salt at 100°, and was connected through a condenser, C, to a water-jacketed nitrometer, D. A current of air-free carbon dioxide was periodically passed through the solution, and the liberated nitrogen was collected over concentrated aqueous potassium hydroxide. In decomposition at high temperatures a condenser is placed between the tube containing the solution and the water-jacketed azotometer. By the use of the stream of inert gas it is possible to overcome the difficulties met with by earlier investigators. Thus, by means of a control experiment,

<sup>1</sup> *J. Chem. Soc.*, 1920, 117, 1446.

<sup>2</sup> *Trans. Chem. Soc.*, 1925, 127, 2936, and 1929, 134, 815.

the time necessary for the solution to acquire the temperature of the thermostat is determined. A thorough sweeping with carbon dioxide expels the nitrogen formed during this time, so that the true starting-point can be determined. Further, no allowances are necessary for the expansion of the solution and air in the apparatus.

As an example of the stability of these compounds under the conditions of the experiment the following figures for the diazonium chloride from 4-amino-1-phenyl-3:5 dimethyl-pyrazolone are given. After 5 hours heating at 100°, approximately 45 per cent of the possible amount of 'diazo' nitrogen is evolved; after 10 hours, about 70 per cent, and after 20 hours less than 90 per cent. At this stage the rate of gas evolution is very small (0.2 ml. per hour), indicating that secondary reactions have taken place. During the main period of the experiment the decomposition of the diazonium chloride followed the course of a unimolecular reaction. The decomposition of the diazonium nitrate closely resembles that of the chloride, but, in the

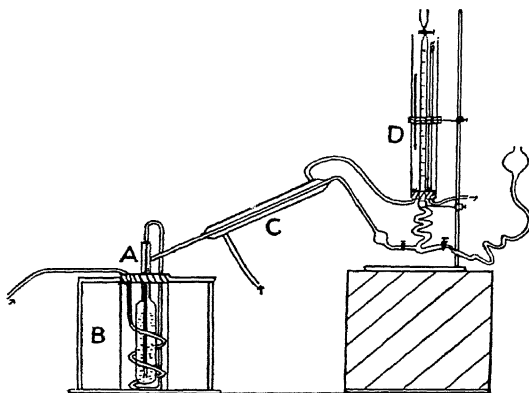


FIG. 35 (XIII)

case of the sulphate, however, the reaction is more rapid at the beginning, and the total evolution of gas smaller, showing increased secondary reaction. The anion, in some cases therefore, appears to influence the rate of decomposition, unlike the results with benzenoid diazonium salts.

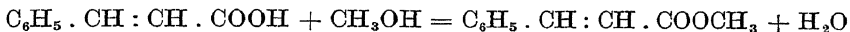
*Formation of Diazonium Salts.* The velocity of formation of diazonium salts has also been studied by Reilly and Bastible.<sup>1</sup> The rate of formation of diazonium salts was ascertained by estimating the amounts of nitrous acid present at varying intervals in a reacting mixture of definite amounts of base and sodium nitrite and mineral acid. The quantity of nitrous acid found was a measure of the amounts of the diazonium salts which were formed in certain time intervals, and so was a measure of the rate of the reaction.

Owing to the very rapid formation of diazonium salts in concentrated solutions, very dilute solutions were employed, the reaction being carried out in N/1,000 solutions, and the estimations made in N/100,000 solutions.

<sup>1</sup> *Sci. Proc. Roy. Dub. Soc.*, 1926, 18, 28, 343.

The effect of this dilution is to retard greatly the rate of the reaction, and so render it capable of more accurate measurement. The method of procedure closely followed that employed by Hantzsch and Schumann for aniline, except that the colorimetric estimation of nitrous acid, instead of being made in ordinary standard Nessler tubes, was carried out in a modified Klett Bio-colorimeter of the Duboseq type. Potassium iodide was used in preference to zinc iodide, as this latter reagent is extremely sensitive, and is influenced by the presence of even traces of impurities. The method of working with the Klett instrument is described in the chapter on Colorimetry. In the improved method of Reilly and Drumm<sup>1</sup> the rates were calculated by direct measurement of the amount of diazonium salt present at various intervals of time: the diazonium solution was coupled with an alkaline solution of Schaeffer's acid, and the solution of the resulting azo-dye was matched in a colorimeter with one similarly and simultaneously prepared from a completely diazotized solution of the amine.

#### (4) The Esterification of Cinnamic Acid in the Presence of Hydrochloric Acid :



Methyl alcohol is purified by refluxing with 1 per cent of calcium turnings (a calcium chloride guard-tube being placed in the end of the condenser to prevent access of moisture). Vigorous boiling is continued until the deposit becomes nearly white and the alcohol is then distilled into a dry receiver (CaCl<sub>2</sub> tube). The portion which comes over at constant temperature is again refluxed with 0.5 per cent of calcium turnings and is distilled into the dry flask which is to be used for the solution of the hydrochloric acid. The flask is weighed first and then again when about 250 ml. have been distilled into it. Carefully dried hydrochloric acid gas is next passed in until the gain in weight corresponds to that of a solution slightly more concentrated than 0.1 N. The concentration of the solution is determined by titration with standard barium hydroxide, using phenolphthalein as indicator, and is adjusted to exactly 0.1 N strength by the addition of pure methyl alcohol.

1.48 grams of pure dry cinnamic acid are weighed out and made up to 100 ml. in a measuring flask with pure methyl alcohol. This solution is also titrated with barium hydroxide. The two solutions are now placed in the thermostat at 25° and left for 20 minutes. After this time 70 ml. of the cinnamic acid solution are run into a dry flask held in the thermostat and then 70 ml. of the hydrochloric solution are added. The time is noted as the zero time and the mixture is shaken; 30 ml. of the mixture is pipetted into each of four bottles, which are then replaced in the thermostat. At the end of each period of 2 hours from the zero time, one bottle is removed and its contents are titrated with the standard barium hydroxide. Each 30 ml. of the mixture contains 15 ml. of the cinnamic acid solution and 15 ml. of the hydrochloric acid solution. The number of millilitres of barium hydroxide required by the cinnamic acid at the start can be calculated from the preliminary titrations. This gives  $a$  in the equation;  $a - x$  at the time  $t$  is obtained by subtracting, from the number of millilitres of barium hydroxide solution required to neutralize the 30 ml. of mixture at the time  $t$ ,

<sup>1</sup> *J. Chem. Soc.*, 1935, 146, 873.



the number of millilitres known from the preliminary titration to be necessary for the 15 ml. hydrochloric acid solution which are present in the mixture. Using these values in the unimolecular-law equation the velocity constant is obtained. In this case the normality of the hydrochloric acid in the mixture is 0.5; if the velocity constant is divided by this factor we obtain the constant called the esterification constant for normal hydrochloric acid.

**(5) The Decomposition of Hydrogen Peroxide by means of Colloidal Platinum**

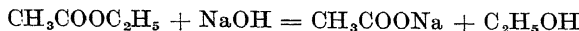


A solution of colloidal platinum can be prepared by Bredig's method. Two pieces of stout platinum wire (2 mm.) are welded to thick copper wires. Pieces of glass tubing are fitted over the wires so that they can be handled; the platinum of course projects from the ends of the glass tubes. The wires are then connected to the lighting circuit in series with a resistance to cut the current down to 5 amps. 20 ml. of conductivity water are placed in a dish and cooled by means of ice (externally). The platinum wires are brought into contact below the surface of the water and then separated 1 or 2 mm. thus establishing a short arc; during the arcing, colloidal (and some larger) particles of platinum are driven off from the platinum. The arc persists for a short time only, and must then be re-made. This is continued for 10 or 15 minutes, and the solution is filtered to separate the coarse particles. 50 ml. of 20-volume hydrogen peroxide are diluted to 500 ml. with distilled water; 250 ml. of this solution are placed in a flask in the thermostat and left for 20 minutes. 10 ml. are then removed, excess of dilute sulphuric acid added, and the mixture titrated with N/10 potassium permanganate. 5 ml. of the colloidal platinum solution are added and the time noted. The initial concentration of the peroxide solution is given by the number of millilitres of N/10 permanganate used, multiplied by  $\frac{240}{245}$ .

2 minutes after the start remove 10 ml. of the mixture, run it into excess of dilute sulphuric acid and titrate, noting the time of starting and the time of completing the titration and recording the mean of these two as the time of the titration. Repeat at intervals of five minutes. The concentration at any time  $t$  is proportional to the number of millilitres of permanganate required, so that these quantities can be inserted directly into the equation.

## BIMOLECULAR REACTIONS

**(1) Saponification of Ethyl Acetate by means of Sodium Hydroxide :**



The following solutions are required : N/60 ethyl acetate, N/40 sodium hydroxide free from carbonate, N/20 hydrochloric acid, and N/20 barium hydroxide. All solutions must be made up with distilled carbon-dioxide-free water. The ethyl acetate is redistilled and the middle fraction taken; 1.467 grams are made up to a litre.

The sodium hydroxide is made up from metallic sodium, a piece of the metal of more than the weight required is taken, the oil removed from its

surface and the outer layers cut off with a clean knife. The metal is then supported on a nickel gauze funnel over a platinum dish on a stand. This is covered as shown in Fig. 36 (XIII) by a bell-jar standing in a dish of water containing caustic soda; the top of the bell-jar is closed by a calcium chloride tube having its lower end bent so that no liquid can drop therefrom into the funnel or platinum dish. The sodium is thus in a moist atmosphere free from carbon dioxide, and it gradually dissolves and the caustic soda so produced drops into the platinum dish. When it has all dissolved the contents of the dish are made up to the required volume with carbon-dioxide-free water; the solution is then titrated against the standard acid and diluted with carbon-dioxide-free water to  $N/40$ . Two 750-ml. conical flasks of Jena glass are steamed out and dried. By means of pipettes 250 ml. of ethyl acetate solution are placed in one and 250 ml. of caustic soda in the other. Paraffined corks or glass stoppers are inserted and the flasks placed in the thermostat, where they are left for 20 minutes. The alkali is then added as quickly as possible to the ester solution and the mean time taken as the zero. The alkali remaining in the flask is washed down the sides and titrated with hydrochloric acid. This enables us to calculate the exact amount of alkali which was added to the 250 ml. of the ester, and also the alkali and ester concentrations of the resulting mixture (which is a little less than 500 ml. in volume). After 3 minutes 50 ml. of the mixture are withdrawn and run into 20 ml. of the  $N/20$  hydrochloric acid solution, which stops the reaction. The time of the start and finish of the delivery of the solution from the pipette is taken and the mean taken as the time to be recorded. The excess of hydrochloric acid is titrated with  $N/20$  barium hydroxide. The 20 ml. of acid are used by  $x$  ml. of barium hydroxide and  $y$  ml. of sodium hydroxide;  $x$  has been determined so that  $y$ , the caustic soda left in the reaction mixture, is calculated; knowing how much was originally present one can calculate the amount of sodium hydroxide used up and so the amount of ester used up and the amount of each left.

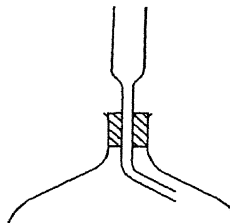


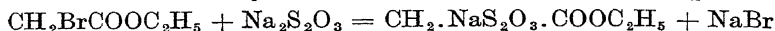
FIG. 36 (XIII)

Further titrations are made at the end of 5, 10, 15, 30, 60, and 100 minutes, and the final titration 24 hours later.

**Results.** An example of Warder's results is given, when both substances were initially at a temperature of  $26^\circ$  and at a concentration of  $N/50$ :

Time in minutes	Alkali still remaining in ml. of $N/8$ acid required for 100 ml.	K
5	10.24	5.625
15	6.13	5.37
25	4.32	5.405
35	3.41	5.27
55	2.31	5.385
120	1.10	5.645

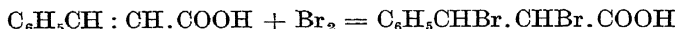
The above measurement presents certain experimental difficulties due to the difficulty of preparing sodium hydroxide free from carbonate and the risk of absorption of carbon dioxide from the air during the reaction.<sup>1</sup> The reaction between ethyl bromoacetate and sodium thiosulphate :



is free from these disadvantages. It is very rapid in dilute solution. It can be followed by removing a portion of the reacting mixture from time to time and titrating with N/100 iodine solution, which only reacts with the unaltered thiosulphate. The experiment can be carried out with very simple apparatus. The following instructions give all essential details for the determination :

300 ml. of an approximately 0.17 normal solution of sodium thiosulphate at 25° is added to an equal volume of the dilute aqueous solution of ethyl bromoacetate at 25° in a 750-ml. flask. The flask is stoppered and the reaction allowed to proceed at 25°. At first every 5 minutes and then every 15 minutes 50 ml. of the reaction mixture is removed and titrated rapidly with standard iodine solution (N/100 approx.), using starch as indicator. Make 8 such titrations and after 5-6 hours (or overnight) a final titration to determine the excess of thiosulphate remaining. Determine the initial concentration of the thiosulphate by titration with iodine and determine the initial concentration of bromoacetate in the reaction mixture from the amount of thiosulphate eventually used up.

## (2) The Bromination of Cinnamic Acid :



This reaction is sensitive to light, so that either the thermostat must be in a dark room or the solution must be mixed in the dark room and transferred to amber-coloured bottles in which it can be kept in the thermostat and only again transferred back to colourless bottles for the titration.

Carbon tetrachloride is purified by washing with sulphuric acid, water, sodium hydroxide, and again water ; it is then allowed to stand over calcium chloride and is finally distilled from phosphorus pentoxide.

The bromine must be pure ; it is shaken with concentrated sulphuric acid, and after separation is frozen by means of ice and calcium chloride ; the solid bromine is separated, melted and again frozen until the melting-point becomes constant (— 7°) ; 1.233 grams of cinnamic acid are made up to 250 ml. with carbon tetrachloride and 1.333 grams of bromine are made up to the same volume with the same solvent. These solutions are accurately standardized, the acid with standard barium hydroxide (N/10), using phenolphthalein as indicator, and the bromine by the addition of excess of aqueous potassium iodide solution and titration of the liberated iodine with decinormal sodium thiosulphate, using freshly prepared starch solution as indicator. 20 ml. of the bromine solution are added to each of six stoppered bottles in the dark room and then 20 ml. of the acid solution. The bottles are stoppered and transferred to the thermostat ; one bottle is removed and its contents titrated by adding potassium iodide solution in excess and then thiosulphate. The concentration of the free bromine remaining is thus found, and since the initial concentration (N/60) is known,

<sup>1</sup> Slaton, *Trans. Chem. Soc.*, 1905, 87, 484.

the amount of bromine used can be determined. Each molecule of bromine used corresponds to a molecule of cinnamic acid used, so that, since the initial concentration of this is known, the amount used can be calculated. If the initial concentrations of the two substances were the same ( $N/60$ ) the calculation becomes very simple, since

$$\frac{dx}{dt} = K(a - x)^2$$

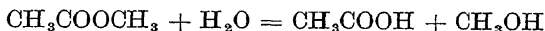
and

$$K = \frac{1}{t(a - x)a}$$

where  $a$  is the number of millilitres of thiosulphate required for the original solution at the start,  $a - x$  is the number of millilitres required after time  $t$ , and  $x$  is the difference of these two.

**Hydrolysis of Salt of Organic Base.** As examples of practical applications of reaction velocities we may take the determination of the degree of hydrolysis of urea hydrochloride.

Methyl acetate is hydrolysed by water according to the equation



and this reaction is accelerated by acids. For a given acid the velocity constant divided by the normality of the acid is an approximate constant; if this value has once been determined it can be used to find the normality of the acid. Now when urea hydrochloride is brought into the presence of water it is partially hydrolysed so that the solution contains some free hydrochloric acid; the urea hydrochloride solution will thus act as a catalyst on the methyl acetate reaction and so enable us to find the concentration of the free hydrochloric acid.

Methyl acetate is distilled and the bottle containing the distillate placed in the thermostat.  $N/2$  hydrochloric acid is prepared and 100 ml. placed in each of two 250-ml. flasks in the thermostat. To one of these flasks 1.5 grams of urea is added so that this becomes an  $N/2$  solution of urea hydrochloride. The  $N/2$  hydrochloric acid should be titrated with barium hydroxide first. Then 5 ml. of methyl acetate are added to the flask containing the acid alone, the contents are quickly mixed, and 5 ml. are withdrawn and titrated at once with barium hydroxide solution. The preliminary test will show how much baryta solution will be required, remembering that the acid has been diluted 5 per cent by the methyl acetate; almost all the baryta can be run in at once and so the titration completed quickly; the mean time is noted. 5 ml. of the methyl acetate can then be added to the urea hydrochloride solution and the same procedure followed. Similar titrations are made at intervals of 10, 20, 30, 40, 60, 120 minutes, and 48 hours, and the velocity constants are calculated from the number of millilitres of baryta and the time, since the reaction is followed by the increase in acidity due to the liberation of acetic acid.

Now, if  $k_1$  is the value found for the velocity constant for hydrochloric acid alone and  $k_2$  is the value for urea hydrochloride, the fraction of urea hydrochloride hydrolysed in an  $N/2$  solution is  $h = \frac{k_2}{k_1}$ .

*Strengths of Acids.* The same reaction can be used to find the relative strengths of acids since the catalysis is actually proportional to the hydrogen ion concentration. We have then, for example, to take 100 ml. each of N/2 hydrochloric acid and N/2 sulphuric acid, add to each 5 ml. of methyl acetate, determine the velocity constants as above, and the relative strengths of the acids used will be

$$\frac{\text{HCl}}{\text{H}_2\text{SO}_4} = \frac{k_{\text{HCl}}}{k_{\text{H}_2\text{SO}_4}}$$

(1) **Determination of the Order of a Reaction.** The rate of reaction is measured by suitable means at given intervals of time, and the results substituted in the equations for the velocity constant for first, second, &c., orders. Of the values of  $k$  so obtained one series will usually show more constancy than the rest. The method is unsatisfactory when complicating side reactions occur.

(2) **van't Hoff's Differential Method.** If the differential  $-\frac{dC}{dt}$  can be measured with different initial concentrations  $C_1$  and  $C_2$ , and the number of molecules taking part in the reaction is  $n$ ,

$$-\frac{dC_1}{dt} = kC_1^n$$

$$-\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms and subtracting,

$$n = \frac{\log \frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2}$$

The differential  $\frac{dC}{dt}$  may sometimes be obtained with sufficient accuracy from the small finite differences in time and concentration  $\frac{\Delta c}{\Delta t}$ .

(3) **The Method of Finding the Times required for Equal Fractional Decreases of Concentration.** Two experiments are made with respective initial concentrations of  $C_1$  and  $C_2$ :

$C_1$  decreases to  $C_1'$  in time  $t_1$

$C_2$  decreases to  $C_2'$  in time  $t_2$

$C_1$  and  $C_2$  are so chosen that

$$\frac{C_1' - C_1}{C_1} = \frac{C_2' - C_2}{C_2}$$

Then  $\left(\frac{C_2}{C_1}\right)^{n-1} = \left(\frac{C_2'}{C_1'}\right)^{n-1}$  (Ostwald)

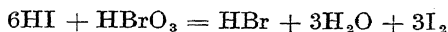
and if the action follows the same course throughout

$$n = 1 + \frac{\log t_1 - \log t_2}{\log C_2 - \log C_1}$$

(4) **Ostwald's Isolation Method.** From the equation

$$-\frac{dC}{dt} = k(C_1^{n^1} \times C_2^{n^2} \times C_3^{n^3})$$

if  $C_2$  and  $C_3$  are made very large compared with  $C_1$  the former may be regarded as constant and  $-\frac{dC}{dt} = kC_1^{n^1}$  so that the exponent  $n^1$  can be determined. In a similar way  $n^2$  and  $n^3$  are obtainable. As an example we may take the determination of the order of the reaction of hydriodic acid on bromic acid :



Decinormal solutions of potassium iodide, potassium bromate, and hydrochloric acid are required, and an N/100 solution of sodium thiosulphate.

25 ml. of iodide, 100 ml. of acid and 100 ml. of water are placed in a 300-ml. conical flask in the thermostat, and in another flask 25 ml. of bromate. When the solutions have had time to acquire the temperature of the thermostat they are mixed and the time is noted. At intervals of 2, 3, 5, 7 and then by intervals of 10 minutes, 25-ml. portions of the reaction mixture are withdrawn, poured into 50 ml. of ice water (to slow the reaction), the mean time being recorded, and then titrated with thiosulphate. A second mixture is prepared in a similar way, containing 50 ml. of iodide, 200 ml. of acid, and 200 ml. of water, and to this 25 ml. of bromate are added and the reaction is followed as before by means of thiosulphate titrations. In the second case the concentration of bromate is half that in the first, the other concentrations remaining the same.

In each case plot the number of millilitres of thiosulphate against time. When the reaction is complete 25 ml. of thiosulphate will be required for 25 ml. of reaction mixture, so that from the curves we can determine the time in each case required for one-third of the iodide to be decomposed. If these times are  $t_1$  and  $t_2$ , and since the reaction mixtures contained

	I				II			
KI	0.01	gram	equivalent	per litre	0.01	gram	equivalent	per litre
KBrO <sub>3</sub>	0.01	"	"	"	0.005	"	"	"
HCl	0.04	"	"	"	0.04	"	"	"

the products of the concentrations are as 2 : 1 ; so

$$n = 1 + \frac{\log t_1 - \log t_2}{\log 1 - \log 2}$$

A second value for  $n$  can be found by taking the times from the curves corresponding to half transformation, i.e. 12.5 ml. of thiosulphate.

**Calculation of End-point.**—Assuming  $a$  is the initial concentration, and  $x$  the concentration at any time  $t$  after the commencement of a reaction. Then for a mono-molecular reaction :

$$K = \frac{1}{t} \log \frac{a}{a-x} \quad (1)$$

and for a bimolecular reaction with equal concentration of reacting substances

$$K = \frac{1}{t} \frac{x}{a(a-x)} \quad \dots \quad (2)$$

Obviously the final reading  $x^\alpha$  corresponding to  $t = \alpha$  is proportional to  $a$ , so that equation (1) and (2) may be written in the form:

$$K = \frac{1}{t} \frac{x}{x_\alpha - x} \quad \text{and} \quad K = \frac{1}{t} \frac{x}{x_\alpha(x_\alpha - x)}$$

In either of these cases a value may be obtained for  $x_\alpha$ , by observing  $x$  at two different times  $t_1$  and  $t_2$  during the progress of the reaction. This is the case of the bimolecular reaction

$$K = \frac{1}{t_1} \frac{x}{(x_\alpha - x_1)} \quad \text{and} \quad \frac{1}{t_2} \frac{x}{x_\alpha - x_2}$$

which leads to a value for  $x_\alpha$

$$x_\alpha = \frac{x_1 x_2 (t_2 - t_1)}{x_1 t_2 - x_2 t_1}$$

For the monomolecular reaction equation (1) may be written  $e^{kt_1} = \frac{x_\alpha}{x_\alpha - x_1}$  and at any subsequent time  $t_2$ ,  $e^{kt_2} = \frac{x_\alpha}{x_\alpha - x_2}$ . Combining:

$$\frac{x_\alpha - x_1}{x_\alpha - x_2} = \frac{t_1}{t_2}$$

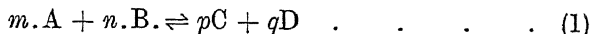
If  $\frac{t_1}{t_2} = \frac{1}{2}$ , this equation leads to a value for  $x_\alpha$  in terms of  $x_1$  and  $x_2$

$$x_\alpha = \frac{x_1}{2 \left( 1 - \frac{x_2}{x_1} \right)}$$

The above method of calculating  $x_\alpha$  was worked out initially by Teegan, who also adapted it to reactions of a higher order. In the latter cases the calculations become complex. The method has been applied for the lower orders to the study of the rate of formation of diazonium salts.

## SECTION 6: MASS ACTION

**The Equilibrium Constant.** If a chemical reaction in a homogeneous system, either for example in the gas phase or in dilute solution, can be represented by the equation



when equilibrium has been reached, the law of Mass Action of Guldberg and Waage tells us that the relation

$$\frac{[A]^m \cdot [B]^n}{[C]^p \cdot [D]^q} = K_c \quad . \quad . \quad . \quad . \quad (2)$$

will hold, where  $[A]^m$  means the concentration in gram molecules per litre of the substance A raised to the power of  $m$ ,  $m$  being the number of molecules of A which occurs in the equation representing the reaction.

$K_c$  is called the equilibrium constant at constant volume. It is a constant which is characteristic for each reaction and which varies only with the temperature.

In the case of gas reactions it is often more convenient to use the partial pressures  $p_A$ ,  $p_B$ , &c., of the various components of the system; the equation then becomes

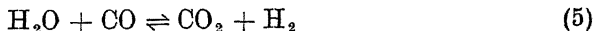
$$\frac{p_A^m \cdot p_B^n}{p_C^p \cdot p_D^q} = K_p \quad (3)$$

where  $K_p$  is the equilibrium constant at constant pressure.

The two constants are related by the equation

$$K_p = K_c(RT)^{m+n-p-q} \quad . \quad . \quad . \quad . \quad (4)$$

**The Equilibrium Constant for Water Gas.** A relatively simple gas reaction which can be used to test the law of mass action is that represented by the equation



The equilibrium constants for this reaction are given by

$$\frac{[H_2O] \cdot [CO]}{[CO_2] \cdot [H_2]} = K_c = \frac{p_{H_2O} \cdot p_{CO}}{p_{CO_2} \cdot p_{H_2}} = K_p = K \quad . \quad . \quad . \quad (6)$$

Equation (5) shows that the reaction produces no change in the total number of molecules, so that it follows from equation (4) that the equilibrium constants at constant volume and constant pressure have the same value.

The method of carrying out the experiment consists in introducing measured volumes of carbon dioxide and hydrogen into the reaction vessel, causing them to react at a certain high temperature and analysing the resulting gas mixture.

The necessary high temperature is provided by a platinum wire which



can be heated to a bright red heat by means of an electric current. The hot platinum also acts as a catalyst for the reaction and hastens the attainment of equilibrium.

The reaction occurs so slowly at the room temperature that it is undetectable, but at a red heat in the presence of the platinum it proceeds with great rapidity. The products of the reaction are removed from the neighbourhood of the catalyst by their own rapid motion at the high temperature and on reaching the colder parts of the apparatus are themselves cooled so that the reaction stops. By this process the equilibrium is said to be 'frozen'.

If the reaction products were cooled slowly in the neighbourhood of the catalyst a fresh equilibrium would tend to be set up at each temperature and the composition of the final mixture would be very different from that which it had at the high temperature: it is only this method of 'freezing the equilibrium' which enables us to get the values corresponding to the high temperature.

In studying any case of equilibrium in a homogeneous system it is of course necessary to ensure that none of the substances leave the system. In this case we must take particular care that none of the water produced leaves the gaseous phase, otherwise the equilibrium set up will not be the one corresponding to our measurements of the amounts of the four gases.

We must avoid, therefore, the condensation of water on the walls of the reaction vessel and on the surface of any confining liquid used.

**Measurement of the Equilibrium Constant for the Water Gas Reaction and to verify the Law of Mass Action.** The apparatus required is shown in Fig. 37 (XIII). F is the glass reaction vessel which has a capacity of 200 ml. The wide mouth at its lower end is closed with the large rubber stopper R and at its upper end is a narrow bore tube with a stopcock S. B is a gas measuring burette with a levelling tube at the side. This burette contains a concentrated salt solution and can be connected to the reaction vessel by the narrow-bore tube  $t_2$ .

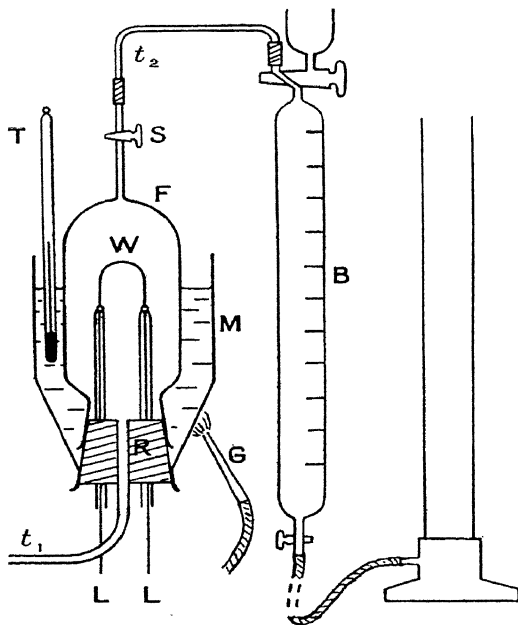


FIG. 37 (XIII)

The lower part of the reaction vessel F is surrounded by the metal

jacket M, this contains water and a thermometer T and can be heated by means of the small gas jet shown at G.  $t_1$  is a tube which passes through the stopper R and connects the reaction flask to a levelling vessel containing paraffin oil: this oil serves as the retaining liquid for the gas in F and it is on this oil surface that we have the danger of condensation of water; this is the reason for the hot-water jacket M. The upper glass parts of F get so hot during the glowing of the platinum wire that there is no danger of condensation there.

W is the platinum wire of length 3-4 cm. and 0.5 mm. diameter; it is sealed into the glass tubes as shown and is joined to the thick copper leads LL. It will be necessary to maintain the wire W at the same temperature in successive experiments, this can be done with sufficient accuracy if we keep constant the voltage across LL and the current in W; a voltmeter (0-20) is therefore connected across LL and in series with W is an ammeter (0-20), a rheostat (2 ohms to carry 20 amps.), a battery of accumulators to give 16 volts and a key.

For the analysis of the gas mixture we require a gas absorption pipette containing 40 per cent caustic potash and a second one containing a solution of cuprous chloride in 8 per cent ammonia: the former to absorb carbon dioxide and the latter for carbon monoxide.

*Method.*—Before starting the experiment the water in M is heated to between 60° and 70° with F full of oil right up to the top. B is then filled with salt solution by raising the levelling tube and about 60 ml. of pure carbon dioxide are introduced. This may be obtained from a Kipp's apparatus and must be washed with water and sulphuric acid and plenty of time allowed for air to be displaced from the wash bottles and the delivery tube. The volume is read off in B at atmospheric temperature and pressure and these are recorded. The carbon dioxide is then transferred to the reaction vessel F. In a similar way about 60 ml. of purified hydrogen is added to B and the volume, temperature and pressure again read; this gas is also transferred to the reaction vessel and the tap S is closed.

The levelling tube is adjusted so that the whole of the platinum wire W lies above the surface of the oil. A small current is passed at first and is gradually raised until the platinum wire is at a bright red heat: this will require 10-18 amps. according to the proportion of hydrogen. This current is maintained for 10 minutes and is then cut off.

Allow the apparatus to cool down for about 10 minutes and then transfer a portion of the gas mixture to B for analysis; about 60 ml. is sufficient. After allowing a further period of 10 minutes for the gas to cool down to the room temperature, measure the volume of the gas mixture in B at atmospheric temperature and pressure. Transfer the gas to the potassium hydroxide absorption pipette and shake, return the gas to B and measure the volume. Repeat until no further diminution in volume is found. Next transfer to the cuprous chloride pipette and shake and again read the volume in B. Here again repeat till the absorption is complete.

The first decrease of volume gives the volume of carbon dioxide; the second gives that of the carbon monoxide and also (from the equation) that of the water if it were still in the state of gas at this temperature and pressure. The residual volume is that of the hydrogen. If there has been

any appreciable change in the temperature during the course of the measurements each gas volume must be reduced to N.T.P. ; otherwise this is not necessary, and each volume can be reduced to what fraction it is of the total volume, and this fraction will be the partial pressure in atmospheres.

Insert the values found in equation (6) and obtain a value for  $K$ .

A check can be obtained on the measurements made by measuring the volume of the residual gas in F. This enables us to calculate the volume of the final mixture less that of the water which has now all condensed. Since the volume of the initial mixture was measured, this contraction gives the volume of the water.

We have then the following checks

ml. of CO = ml. of  $H_2O$  = ml. contraction

Initial volume of  $H_2$  - final volume of  $H_2$  = ml. contraction = ml.  $H_2O$

Initial volume of  $CO_2$  - final volume of  $CO_2$  = CO formed = ml.  $H_2O$

Repeat the experiment once or twice with different initial volumes of carbon dioxide and hydrogen, e.g. 80 ml. of carbon dioxide and 40 ml. of hydrogen, &c.

Since the magnitude of  $K$  is constant only for a given temperature, the maximum temperature of the wire must be regulated to have the same value each time by means of the voltmeter and ammeter.

If the values of  $K$  found in the different experiments agree the equation from which  $K$  is calculated is correct and the law of mass action is verified.

## SECTION 7: STABILITY OF EXPLOSIVES

The chemical testing of explosives for stability is always supplemented by tests of a physico-chemical or physical nature. This applies especially to storage trials at ordinary temperatures or under warm conditions. Such tests investigate whether alterations have taken place in physical properties, e.g. hardening, conglomeration, exudation, absorption of moisture, and in chemical properties, e.g. stability, &c., due to increased chemical reactions. A summary of these and related tests is given below. For more detailed accounts of such tests, see Reilly, *Explosives, Matches and Fireworks*, Gurney & Jackson, London, 1938.

**Density.** The density of gunpowders and similar powders may be obtained by the methods given in Chapter XII, S. 2. The density of blasting explosives in cartridge form may be estimated by weighing and measuring the cartridges. Another approximate method is to measure the displacement of sand. A glass tube is filled with sand and weighed. It is then emptied and a weighed stick of the explosive is inserted. Sand is poured in until the tube is full. The sand is levelled off and the whole is weighed. The apparent density of the sand is determined separately in the same tube.

**Tendency to Segregate.** Mixed explosives may tend to separate to some extent into their ingredients by shaking or by alternations of moisture in the atmosphere. The effect of shaking may be determined by putting a quantity of the explosive into a wide-mouthed bottle, so that the bottle is partially filled. The bottle is corked and shaken in a mechanical shaker for an hour. The explosive is then examined for visible signs of segregation and separate portions may be taken out and examined for differences in ease of ignition, &c. The effect of moisture is ascertained by exposing a sample in a flat dish for alternate periods of 24 hours to moist and dry air and examining after a week for efflorescence of crystals.

Movement of nitroglycerine in a cartridge by gravitation is tested by keeping the cartridge in a vertical position for some weeks at 32°. Portions from the two ends are examined for nitroglycerine content before and after the test, which may be carried out in dry or moist air.

**Exudation.** This refers mainly to nitroglycerine explosives. Exudation is undesirable, as the liquid nitroglycerine which exudes may become exploded by friction or shock. The exudation can be measured by placing a cylinder of the explosive on porous paper in a warm oven and ascertaining the amount of liquid which sweats out. A typical explosive is taken as a control. In one particular test a cylinder is cut from the cartridge, such that the length is about equal to the diameter. The ends are cut flat and the cylinder is placed on a flat surface and secured by a pin. It is then kept at 30° to 33° for 6 days and nights. The cylinder must not decrease

by more than a quarter of its height, and the upper surface must retain its flatness and the sharpness of its edges. Sometimes pressure is applied to facilitate the exudation, and centrifuging has also been applied. To test the exudation due to freezing, the cartridges are frozen and thawed three times. Exudation is also met with in nitro-compounds which form eutectic mixtures.

**Inflammability.** A small sample of the explosive is filled into a glass or paper tube about 2 cm. in diameter. The exposed surface is smoothed, and a slow fuse is brought in contact with it and ignited, to ascertain whether the explosive inflames and whether it burns partially or completely. The test should be repeated on several samples. The ease of inflammation may also be measured by playing a small bunsen flame on to the explosive for a measured time, say 10 seconds. Considerable differences are observed between different explosives. Control samples of known explosives should be included for comparison. Another method is to fasten a small quantity of the explosive to the end of a pendulum which swings through a flame in such a way that the time can be measured.

If the explosive has withstood the test in which it is exposed to the flame from a slow fuse, it is further tested by dropping a portion of 0.5 gram into a red-hot iron basin 12 cm. in diameter. The quantity may be increased to 5 gram if no explosion occurs. The basin must be well cleaned after each test and should be frequently renewed; on the other hand, a new basin does not give quite normal results until it has been used once or twice.

In some cases, larger quantities of a pound or two are burnt in a wood fire to ascertain the degree of danger to which the explosive may give rise in case of fire. The observations should be made under precautions at a safe distance.

**Ignition Temperature.** This is usually determined by placing 0.1 gram of the explosive in a small test-tube, which is then corked and placed in a fusible metal bath at 100°. The temperature is raised 5° per minute until inflammation or explosion occurs. The quantity and rate of heating differ in different countries.

**Sensitiveness to Shock and Friction.** The sensitiveness to blows is measured by the falling weight test. The explosive must be finely divided and well dried. A small portion is spread in a thin layer on an anvil. A bolt rests on the explosive and a cylindrical weight is allowed to fall upon it from a measured height. If explosion occurs the test is repeated with a lower height of fall until the mean height is found at which explosion just occurs. A standard explosive which can be obtained in pure condition, such as picric acid, is taken as a control. Considerable difficulty has been met with in obtaining reproducible results. An improved method was introduced by Rotter<sup>1</sup> in which the results of each impact are evaluated, not by personal judgment but by a quantitative measurement of the gas produced by the decomposition of the explosive. A number of typical results are quoted by Robertson. The sensitiveness to friction may be tested qualitatively by rubbing a small portion of the explosive vigorously in an unglazed mortar with an unglazed pestle. A useful test is to strike a glancing blow with a mallet, the explosive being laid on anvils of different

<sup>1</sup> Cf. Robertson, *J. Chem. Soc.*, 1920, 117, 16.

materials. Howell's<sup>1</sup> apparatus consists of a steel anvil with grooves to hold the explosive (7 gram), and a swinging shoe which is allowed to fall with a circular motion from various heights.

**Lead Block Test.** This is one of the oldest tests for the explosive power, and is still widely used. The explosive is fired in a cavity in a cylindrical lead block. The cavity becomes enlarged and the increase of volume is taken as a measure of the power. Standard conditions were laid down at the Fifth International Congress of Applied Chemistry. The lead block is cylindrical and is 200 mm. in height and 200 mm. in diameter. The cylindrical cavity is 125 mm. deep and 25 mm. in diameter. 10 grams of explosive wrapped in tinfoil is taken for the test, and tamped with sand. The charge is fired by a detonator, and the expansion is measured by finding the volume of water necessary to fill the cavity. The original capacity of the bore is deducted and allowance should be made for the expansion due to the detonator. The purity of the lead and the temperature of casting of the blocks affect the results to some extent. The significance of the test is dealt with by Naoum.<sup>2</sup>

**Ballistic Pendulum.** A heavy mortar is suspended from a bearing and a stemmed shot is fired into it from a steel gun. The degree to which the pendulum swings gives a measure of the energy imparted to it. The weight of the mortar and height of suspension differ in different countries, e.g. at Rotherham 5.025 tons at 92 inches, in America 14.1 tons at 89.75 inches. The gun is brought to a measured distance from the mortar and fired electrically. Charges of  $\frac{1}{4}$  to  $\frac{1}{2}$  lb. of explosive are used, and a standard explosive is taken for comparison.

In another method a heavy mortar, firing at an elevation of 30°, is used. The explosive is detonated by means of a slow fuse and propels a projectile weighing 15 kilograms. The distance to which this is thrown is measured.

**Brisance Meter.** In using this apparatus, the violence of the explosive effect is measured by the crushing of a metal cylinder. The explosive is detonated on a steel plate, covered by two lead discs for protection. The steel plate is 2 cm. thick, weighs 320 grams and is supported by a piston fitting into a hollow steel cylinder. The lower end of the piston rests on a copper cylinder supported by the steel base. The detonation of the explosive transmits a pressure through the piston to the copper cylinder, and crushes it to an extent which can be measured. The degree of crushing is used to compare the brisance of different explosives.

**Rate of Detonation.** Two methods are in use. In the direct method, the time of detonation of a measured length of a column of explosive is determined. This necessitates the accurate measurement of very short time intervals, which is effected by means of a rapidly rotating drum fitted with a speed recorder. The column of explosive is fitted with wires at a fixed distance apart, generally 1 metre. The rupture of the wires gives rise to induction sparks, which give spots on the smoked surface of the drum. By measuring the distance between the spots, the rate of detonation can be calculated. The velocity depends upon the diameter of the train of explosive

<sup>1</sup> *U.S. Bureau of Mines, Tech. Paper, 234.*

<sup>2</sup> *Z. ges. Schiess- u. Sprengstoffw., 1932, 27, 181, 229, 267.*

up to a limiting value, the degree of confinement, the density, and the method of initiation.

In Dautriche's method the explosive to be tested may be in cartridges or compressed into a tube A containing the high explosive, and a detonator is inserted at one end (Fig. 38 (XIII)). Two other detonators are inserted into the sides of the tube at a known distance apart, and connected to a

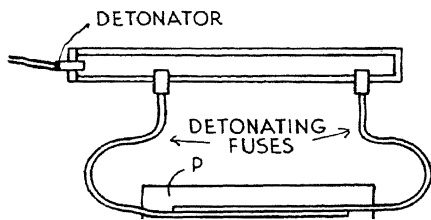


FIG. 38 (XIII)

loop of the detonating fuse. When the explosive is detonated the detonation is transmitted successively to the two ends of the detonating fuse, and the two waves meet at a point depending on the rates of detonation of the main explosive and of the explosive in the detonating fuse. The point at which the waves meet is ascertained by the indentation of a slab of lead P on which the detonating fuse lies.

The sensitiveness to detonation is determined by subjecting the explosive in its usual form (e.g. in cartridges) to the action of detonators of different intensities. These are fired electrically, and the effect on the explosive is observed.

In order to ascertain the propagation of detonation, two cartridges are placed end to end on the ground at a certain distance apart, and one of them is detonated. By varying the distance it can be ascertained at what distance the first cartridge is able to detonate the second.

**Length and Duration of Flame.** These are of importance in connexion with the ignition of fire-damp, &c. The measurements are made photographically. A sensitive film is fixed to a drum, which is rotated at a known speed, and the flame is photographed through a narrow slit in such a way that the height of the image shows the length of the flame and the breadth shows its duration.

**Testing of Detonators.** A review of the methods used for detonators is given by Kast and Haid.<sup>1</sup> The initiating action may be determined by the Esop and Wöhler tests in which the detonator is fired in contact with an explosive which has been partially deadened by the addition of an inert substance. Tests are also made to determine the limiting charge of a detonator composition, which just suffices to bring about detonation. In the 'Sand test' of the U.S.A. Bureau of Mines, a detonating charge is exploded in a mass of carefully graded sand and the degree of pulverization caused by the explosion is measured. In the 'Nail test' the detonator is attached by means of wire to a nail, the two being parallel and the lower end of the detonator being level with the centre of the nail. The power of the detonator is measured by the degree of bending of the nail. Standard nails must be used for the test.

The Trauzl test is sometimes used with a smaller lead block. The indentation of a lead plate is also frequently made use of.

**Stability Tests.** Nitric esters undergo gradual decomposition on

<sup>1</sup> *Z. ges. Schiess- u. Sprengstoffw.*, 1924, 19, 146.

storage. Stability tests are therefore necessary as a control of the safety of explosives of this type. The tests are applied during manufacture and to the finished explosive; and they may also be applied at intervals during storage, especially in hot climates.

The usual procedure in stability tests is to subject a sample of the explosive to a raised temperature in order to increase the rapidity of the decomposition and obtain a quick indication of the stability. After heating at constant temperature for a certain length of time, the degree of decomposition is measured by one of the following methods:

- (1) By indicators depending on the action of nitric peroxide
- (2) Direct observation of brown fumes
- (3) Measurements of spontaneous heating.
- (4) Methods depending on the explosion of the sample
- (5) Quantitative estimations of decomposition products
- (6) Loss of weight
- (7) Gasometric methods
- (8) Acidity measurements

The most reliable procedure is to carry out a heating trial at a temperature not far removed from the temperature of storage, but this necessitates a prolonged trial in order to bring about a measurable degree of decomposition, and is not always practicable. For details of these tests, see Reilly, *Explosives, Matches and Fireworks*, 1938.

For high explosives the most suitable stability test is that known as the vacuum stability test. In the Farmer test<sup>1</sup> a weighed amount of the dried explosive is placed in a test-tube of the type shown in Fig. 39 (XIII). The manometer is attached and the tube evacuated and placed in a thermostat. The temperature of the test varies from 80° to 180°, according to the explosive under test. The progress of the decomposition is followed by readings of a mercury manometer.

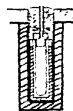


FIG. 39 (XIII)

<sup>1</sup> *J. Chem. Soc.*, 1922, 121, 174.





## SUGGESTIONS FOR FURTHER READING

### INTRODUCTION

THE output of articles and books on physico-chemistry has now reached such enormous dimensions as to preclude any attempt to compile a list which could be dignified by the term 'bibliography'. Some general indications of the relevant material will be found in the following:

Crane and Patterson. *Guide to the Literature of Chemistry*, Wiley, 1927.

Soule. *Library Guide for the Chemist*, McGraw-Hill, 1938.

Olsen. *Van Nostrand's Chemical Annual*.

The object of this section—which is a new feature of the present edition—is much more modest. This book, having to be kept within manageable limits, could not deal exhaustively with each of the included topics; it was in fact written to provide that general conspectus which is necessary even for the student who intends to specialize in one department. While therefore the authors and their collaborators had inevitably to aim at the least common denominator and to spread their treatment with some effort at uniformity over a wide field, many readers will desire to pursue further the study of selected portions. It is hoped that the references here given will be of help to such students and will enhance the value of the various chapters. It is to be understood that no attempt at a complete bibliography is intended. The object of the section is to give references to books—and to a lesser extent, articles—which will enable the reader to acquire further knowledge of the subject-matter of any chapter in which he is specially interested. Needless to say, no serious student is exempted from keeping in touch with recent literature as recorded, say, in *Chemical Abstracts* (British and American) or in *Science Abstracts* (Section A, Physics). Indeed for certain chapters it was considered useless to give special references, as practically every issue of these Abstracts contains references to relevant articles. But for many of the chapters there exist—in addition to the sources cited in the text—convenient monographs which provide more detailed information than it was possible to include in a general treatise. It is hoped that references to the most important and accessible of these are given in the following pages.

As a preliminary, we give a list of the more important collections of empirical data and a list of the outstanding journals.

#### *Physico-Chemical Data*

Kaye and Laby. *Physical and Chemical Constants*. Longmans, 8th ed., 1936.

Lange. *Handbook of Chemistry*. Handbook Publishers, Ohio. 2nd ed., 1937.

Lange's book gives the Physical Constants of over 4000 organic compounds and their reference in Beilstein.

Castell-Evans. *Physico-Chemical Tables*. 2 vols.

- |                           |            |
|---------------------------|------------|
| (1) Chemical Engineering. | } Griffin. |
| (2) Chemical Physics.     |            |

*International Critical Tables of Numerical Data, Physics, Chemistry and Technology*. 7 vols., with index, 1926-33. New York, McGraw-Hill.

Landolt-Bornstein. *Physikalisch-chemische Tabellen*. Berlin, Springer. 5th ed., 1923. Three supplementary volumes (Ergänzungsbande). (1) In 1927. (2) In two parts 1931. (3) In three parts 1935-36.

*Tables Annuelles de Constantes et Données Numériques* (Annual Tables of Constants and Numerical Data). Vol. I (1910) to Vol. II (1931-34), with two volumes

of indices. Published by Hermann, Paris; New York agent, McGraw-Hill. The new series (1931-36) contains some useful monographs, e.g.

No. 4. *Conductibilité thermique (1931-34), Chaleur spécifique (1931-34)*.

No. 10. *Thermochimie (1931-34)*.

No. 15. *Effet Raman (1935-36)*.

No. 18. *Conductibilité des électrolytes (1931-36)*.

No. 27. *Tension de vapeur (1935-36), Lois des Gaz (1935-36)*.

No. 29. *Thermochimie (1935-36)*.

Childs. *Physical Constants*. Methuen, 1934. This pocket book is specially written for students.

Egloff. *Physical Constants of Hydrocarbons*. (In 4 vols.) only Vol. I published to date. A.C.S. Monograph No. 78 with bibliography. Reinhold, 1939.

A report on Symbols for Physico-chemical Quantities, &c., and conventions relating to their use was issued by a joint committee of representative scientific societies in England in 1937. Copies of Report (16 pp.) obtainable from Chemical Society, London.

*Chemisch-technische Untersuchungsmethoden*. Berlin, Verlag Springer. Principal Work (Hauptwerk). 5 vols. 1931-34.

A Supplement (Ergänzungswerk) to this edition, in three parts, has been issued in 1939.

This book has a good bibliography on many sections of physical chemistry.

For a more restricted survey, but covering such sections as: units of measurement, densities, barometric tables, viscosity, thermometry, melting and boiling points, indices of refraction, &c., the following may be consulted:

Fowle (ed.). *Smithsonian Physical Tables*. Smithsonian Institution, Washington. 8th ed., Pub. No. 3171. Revised, 1933.

#### Serial Publications

American Institute of Chemical Engineering, *Transactions*.

British Chemical Abstracts.

Chemical Abstracts.

Chemical Engineering.

Chemisches Zentralblatt

Faraday Society, *Transactions*.

*Fortschritte der Chemie, Physik und physikalischen Chemie*.

Institute of Chemical Engineers, *Transactions*.

*Journal de chimie physique*.

*Journal of Chemical Physics*.

*Journal of Physical Chemistry*.

*Journal of Scientific Instruments*.

*Review of Scientific Instruments*.

*Science Abstracts*; Section A (Physics).

*Zeitschrift für Elektrochemie und angewandte physikalische Chemie*.

*Zeitschrift für physikalische Chemie*.

The above list, while not complete, gives a representative list of important journals of value to the physical chemist. It will be noticed that a number of publications in Chemical Engineering have been included. These periodicals very often contain papers of a physico-chemical nature. Details of the above journals and complete lists of the more specialized journals in physics, chemistry, physiology (which contain physico-chemical data from time to time) may be found in the reference books of Soule or of Crane and Patterson.

#### CHAPTER I. THE LABORATORY

In 1932 the Royal Institute of British Architects approached British Universities and certain kindred institutions in an attempt to obtain some degree of understanding as to what technical arrangements are generally felt to be most desirable in laboratory buildings. A comprehensive questionnaire was circulated to interested parties. A report was published by the Institute in 1933.

- Munby. *Laboratories, Their Planning and Fittings*. Bell, 1931.
- Murray. *The Laboratory: Its Place in the Modern World*. Fenland Press, 1934.
- Edwards. 'Equipment of the Chemical Laboratory', *Chem. Age*, 1939, 40, 317.
- Butcher. 'Planning and Construction of Laboratories', *Chem. Age*, 1939, 40, 317.
- Morteret. 'Equipment for the Chemical Laboratory', *Tech. Ind. Chem.*, 1938, 277, 175.
- Warren. 'Laboratory Apparatus', *Ind. and Eng. Chem. Anal.*, 1939, 11, 574.
- Hull. *Industrial Research Laboratories of the United States, Including Consulting Research Laboratories*. 6th ed., Nat. Res. Council, Nat. Acad. of Science, 1938.
- Lampitt. *Laboratory Organisation*. Inst. of Chem., London, 1935.
- Dunstan. 'The Organisation of an Industrial Research Station', *Chem. Eng. Congress World's Power Conference 1936*, Vol. 4.
- Juschkevitch. 'Research Institutes and Designing Establishments for Chemical Engineering in the U.S.S.R.', *Chem. Eng. Congress World's Power Conference 1936*, 4, 713.

A chart (The Laboratory Emergency Chart) with first-aid information, &c., has been prepared by the Fisher Scientific Co., Pittsburg, Penn., and is useful addition to any laboratory. Up to 1939 over 37,000 copies have been distributed in the United States and Canada.

## CHAPTER II. BASIC MEASUREMENTS

- Charter. *Practical Measurements*. Longmans, 1928.
- Ferry, Silvey, Sherman and Duncan. *Handbook of Physical Measurements* (Vol. I, Fundamental Measurements). Wiley, 2nd ed., 1925.
- Bloch. *Messen und Wägen*. Leipzig, Spamer, 1928.
- Fleury. *Leçons de métrologie générale et appliquée*. Paris, Hermann, *Actualités*, Nos. 236 (1935), 278 (1935), 653 (1938).
- Keleny and Eriksen. *Manual of Physical Measurements*. McGraw-Hill, 6th ed., 1937.
- Prost. *Travaux pratiques de physique. I. Mesures, Chaleur*. Paris, Hermann, *Actualités*, No. 626 (1938).
- Abraham. 'Dividing and Ruling Scales,' *J. Sci. Inst.*, 1939, 7, 205.

### A. Length

1. Sears. 'Our Basic Standards of Measurement', *Sci. Prog.*, 122, 1936.
2. Rolt. *Gauges and Fine Measurements*, Vol. I. Macmillan, 1929.
3. (i) Comparators. (ii) Line Standards of Length. (iii) Gauges. *Dictionary of Applied Physics*. Macmillan, 1923.
4. Berndt. *Grundlagen und Geräte technischer Längen-messungen*. Springer, Berlin, 1929.
5. Perard. *La haute précision des mesures de longueur au laboratoire et dans l'industrie*. Paris, Hermann, *Actualités*, No. 19 (1931).
6. The following specifications of the British Standards Institution relate to Engineers' Measuring Tools:
  - No. 817. Cast Iron Surface Plates and Tables.
  - No. 818. Cast Iron Straight-edges.
  - No. 852. Toolmakers' Straight-edges.
  - No. 863. Steel Straight-edges of Rectangular Section.

### B. Angular Measurement

1. Rolt. *Gauges and Fine Measurements*, Vol. II. Macmillan, 1929.
2. Berndt. *Technische Winkelmessungen*. Springer, Berlin.

### C. Crystal Measurement

- Wychoff. *The Structure of Crystals*, 2nd ed., Chap. II (Reinhold Pub. Co., 1930), deals with crystal measurement. For other references see Vol. II, pp. 340, 575.

D. *Volume*

1. *Tests on Volumetric Glassware*, latest ed. National Physical Laboratory.
2. Jouniaux. *Mesures des volumes liquides*. Paris, Hermann, *Actualités*, Nos. 351-55 (1936).
3. 'The Millilitre', *Nature*. Oct. 19th, 1928.
4. Report on Metric Units of Volume No. 501—1933 British Standards Institution.
5. Report on Standard Temperature of Volumetric Glassware. No. 554—1934, British Standards Institution.
6. Stott and Witherby. *Volumetric Glassware*. 1928.
7. 'Measurement of Volume', *Dictionary of Applied Physics*. Macmillan, 1923.
8. The following specifications of the British Standards Institution deal individually with volumetric glassware of various types :
 

No. 604—1935.	No. 700—1937.
No. 605—1935.	No. 701—1936.
No. 612—1935.	No. 756—1939.
No. 615—1936.	No. 773—1938.
No. 675—1936.	No. 797—1938.
No. 676—1936.	No. 846—1939.
9. The following specifications of the British Standards Institution deal with various types of thermometer :
 

No. 691—1936.	No. 695—1936.
No. 692—1936.	No. 593—1935.

No. 619—1935.

E. *Mass*

1. Reference A1 above.
2. Verification of Weights, Testing of Balances and Determination of Densities. National Physical Laboratory.
3. 'Balances', *Dictionary of Applied Physics*, Vol. III. Macmillan, 1923.
4. Ainsworth. 'Analytical and Microbalances', *Ind. and Eng. Chem. Anal.*, 1939, 11, 572. See also p. 674, S. 4.

F. *Density and Hydrometers*

1. 'Hydrometers and Hydrometry', *Report of World Petroleum Congress*, II, 880. London, 1933.
2. British Standards Institution Publications :
 

No. 733—1937.
No. 718—1936.
No. 734—1937.
3. Reference E2 above.

G. *Time*

1. Reference A1 above.
  2. Sears and Tomlinson. 'A High Precision Chronograph', *J. Scient. Inst.*, 1931, 8, 1.
  3. Scheibe und Adelsberger. *Phys. Zeits.*, 1933, 33, 835.
  4. Scheibe. *Hoch. freq. u. Elek. Akus.*, 1934, 43, 37.
  5. Essen. 'The Quartz Clock', *Occasional Notes of the Royal Astr. Soc.*, 1938. No. 1, p. 7.
  6. Essen. 'A New Form of Frequency and Time Standard', *Proc. Phys. Soc.*, 1938, 50, 413.
  7. Essen. 'The Dye Quartz Ring Oscillator as a Standard of Frequency and Time', *Proc. Roy. Soc.*, 1936, 155A, 498.
  8. Vigoureux. *Quartz Resonators and Oscillators*.
  9. Scheibe. *Piezo-elektrizität des Quarzes*.
  10. Marrison. *Proc. Inst. Rad. Eng.*, 1929, 17, 1103.
  11. Jones. 'Measurement of Time', *Annual Report on Progress in Physics*, Phys. Soc., London, 1937.
- See also Units and Standards of Measurement employed at The National Physical Laboratory. H.M.S.O., 1929.

## CHAPTER III. MEASURES AND UNITS

Unfortunately, discussions on 'dimensions' often deal with peculiar pseudo-mystic ideas, so that they will not help much in extending the treatment in this chapter.

Bridgman. *Dimensional Analysis*. New Haven, 1922.

Everett. *Illustrations of C.G.S. System of Units*. Macmillan, 1902.

Lanchester. *The Theory of Dimensions and its Application for Engineers*. Crosby Lockwood, 1936.

O'Rahilly. *Electromagnetics*. Longmans, 1938.

Porter. *The Method of Dimensions*. Methuen, 1933.

## CHAPTER IV. OBSERVATIONS AND CALCULATIONS

A general treatment will be found in such textbooks as :

Sherwood and Reed. *Applied Mathematics in Chemical Engineering*. McGraw-Hill, 1939.

Mellor. *Higher Mathematics for Students of Physics and Chemistry*. Longmans, 1922.

S. 1. *Errors of Observation and Interpolation*

Whittaker and Robinson. *The Calculus of Observations*. Blackie, 1924.

Brunt. *The Combination of Observations*. Camb. Univ. Press, 1931.

Steffensen. *Interpolation*. Williams and Wilkins, 1927.

For further reading on more recent developments :

Fisher. *Statistical Methods for Research Workers*. Oliver and Boyd, 7th ed., 1938.

Yule and Kendall. *An Introduction to the Theory of Statistics*. Griffin, 11th ed., 1937.

Landau and Lifshitz. *Statistical Physics*. Oxford. Clarendon Press, 1938.

S. 2. *Nomography*

d'Ocagne. *Traité de Nomographie*. Gauthier-Villars, 1921.

Brodetsky. *A First Course in Nomography*. Bell.

Allcock and Jones. *The Theory and Practical Construction of Computation Charts*.

Pitman, 2nd ed., 1938.

S. 3: *Slide Rule*

A book of instructions may be obtained when purchasing a slide rule.

Thompson. *A Manual of the Slide Rule*. Van Nostrand, N.Y.

Pickworth. *The Slide Rule*. Pitman, 17th ed., 1920.

S. 4. *Graphic Methods*

Brunton. *Graphic Methods for presenting Facts*. McGraw-Hill, 1914.

Schultze. *Graphic Algebra*. Macmillan, 1933.

## CHAPTER V. PHASES

Bowden. *The Phase Rule and Phase Relations : Theoretical and Practical*. Macmillan, 1938.

'Symposium on liquid crystals', *Trans. Far. Soc.*, 1933, 29, 881.

Findlay. *The Phase Rule and its Applications*. 7th ed., reprint, Longmans, 1935.

Rhodes. *Phase Rule Studies*. Oxford Univ. Press, 1933.

Rivett. *Phase Rule*. Oxford Univ. Press, 1923.

Volmer. *Kinetik der Phasenbildung. (Die Chemische Reaktion, Band IV.)*, Dresden-Leipzig, 1939.

## CHAPTER VI. MISCELLANEOUS APPARATUS

Many of the references given in connection with other chapters obviously involve descriptions of apparatus. Recent improvements are listed in *Chemical Abstracts* and *Science Abstracts*. The Physical Society (London) publishes a useful catalogue of the annual Exhibition of Scientific Instruments and Apparatus. See also :

Kieser. *Handbuch der chemisch-technischen Apparate*, 1 (1934), 2 (1937), 3 (1939), Springer, Berlin.

Groggins. *Unit Processes in Organic Synthesis*. New York, 1935.

*Practical Hints on Use and Maintenance of Platinum Laboratory Apparatus*. Pub. No. 47, Johnson, Matthey, London, 1939.

Sherrick and Wilson. 'Research on Instrumentation', *Ind. and Eng. Chem.*, 1939, 11, 576.

S. 1. *Thermostats*

Waddle and Imhoff. 'Laboratory Thermo-regulator', *J. Chem. Educ.*, 1938, 15, 4, 191.

Bratton. 'Simple Mechanical Thermo-regulator', *Science*, 1939, 589.

Lalande. *Les thermostats pour les températures moyennes*. Paris, Hermann, *Actualités*, No. 276 (1935).

Stull. 'Semi-micro Calorimeter', *J. Amer. Chem. Soc.*, 1937, 59, 2726.

Christensen and King. 'Thermostat. Range 100° to 250°' (using *o* and *m*-phosphoric acid mixtures), *J. Inst. and Eng. Chem. Anal.*, 1936, 8, 194.

Beadle and Booth. 'Low-temp. Thermostat', *Nature*, 1937, 140, 279.

Wolf and Frahm. 'Calorimeter for Measurement with Liquids of High Vapour Pressure', *Z. phys. Chem.*, A, 1937, 178, 411.

See also *Science Abstracts* (A, Physics) and *British and Amer. Chem. Abstracts*.

S. 2. *Stirrers*

Keyser. 'Laboratory Stirrer', *J. Chem. Educ.*, 1936, 13, 590.

Bertram. 'Stirring under Vacuum', *ibid.*, 1937, 34, 287.

Briggs. 'Mercury Seal for Stirrers', *Ind. Eng. Chem. (Anal.)*, 1937, 9, 196.

Oyama. 'Packing and Mixing of Broken Solids by a Horizontal Shaking Motion', *Inst. Phys. and Chem. Res. (Tokyo) Sc. Paper*, 1933, 839, 1262.

S. 3. *Drying and Evaporating Apparatus*

Pavelka. 'Micro-oven', *Mikrochemie*, 1937, 22, 247.

Walden. 'The Construction of Electric Furnaces', *J. Sci. Inst.*, 1939, 16, 1.

Beaulieu Marconnay. 'The Electrical Heating of Vessels', *Chem. Fabr.*, 1936, 9, 541.

Fairbrother. 'A small High-Temperature Furnace', *J. Sc. Inst.*, 1935, 12, 200.

Trifonov and others. 'Electric Tube Furnaces for High Temperatures' (1600° C.), *Oesterr. Chem. Ztg.*, 1937, 40, 315.

Pring. *The Electric Furnace*. Longmans, 1921.

S. 4. *Balances and Weights*

Manley. 'Balance', *Thorpe's Dict. of Chemistry*, 1937, 1, 587.

Buchan. 'Balance, The Conrady Method of Weighing', *ibid.*, 1937, 1, 387, 613.

Dippel. 'Sensitive Quartz Spiral-Spring Balance', *Chem. Weekblad*, 1937, 34, 317.

Trenner. 'A Gas Density Balance for determining the Absolute Density of Protium-Deuterium Mixtures', *J. Amer. Chem. Soc.*, 1937, 59, 1391.

S. 5. *Accumulators.*

Vinal. *Storage Batteries*. 2nd ed., Wiley, New York, 1930.

Allmand and Ellington. *Principles of Applied Chemistry*. 2nd ed., Longmans, 1924.

Although this book is old the section on accumulators is excellent.

Ibbetson. *Accumulator, Charging, Maintenance and Repair*. 6th ed., Pitman, 1939.

Tobson. *The Battery Book*. Technical Press (London), 1937.

Browne. *The Lead Storage Battery*. 3rd ed., Locomotive Pub. Co., London, 1937.

*Standard Handbook for Electrical Engineers*. McGraw-Hill.

(See also section on Electro-chemistry, Vol. II, Chap. VIII\*.)

## CHAPTER VII. PUMPS

- Klumb. *Electrotech. Zeit.*, 1936, 57, 1445-8; describes modern high-vacuum pumps.
- Archer. *J. Sci. Inst.*, 1936, 13, 161-5. Methods of making joints (metal-glass, &c.) in vacuum apparatus are described.
- Brenschede. *Z. phys. Chem.*, 1936, A178, 75. Describes an electro-magnetic piston pump for laboratory use.
- Mönch. *Chem. Ztg.*, 1936, 60, 465. Gives a review of apparatus and technique employed in high-vacuum work.
- Seiler. *Z. tech. Physik*, 1938, 19, 283. A protective device for vacuum pumps. The cooling water of the pump runs into a cup on a counterbalanced beam. If the water supply fails the beam moves and operates a switch stopping the pump.
- Anderson. *Rev. Scient. Inst.*, 1937, 8, 493. An important variation in de-gassing charcoal traps. The charcoal itself acts as a resistance heater and de-gassing proceeds more quickly.
- Grigorovici. *Zeit. tech. Physik*, 1939, 20, 102. Describes a glass-membrane manometer with mirror arrangement useful over the range 0.1-20 mm.
- Ritter. *Chem. Zeit.*, 1939, 63, 253, 278. Shows advances in industrial pumps for liquids.
- Youtz. *Rev. Scient. Inst.*, 1938, 9, 420. Describes protective device for large vacuum systems to deal with interruption of the mechanical vacuum pump.
- For general references see *Science Abstracts* (A. Physics).

## CHAPTER VIII. VARIOUS OPERATIONS

Such operations as glass blowing, laboratory manipulation and workshop practice generally require more than mere description for successful accomplishment. Under this heading are included the silvering of glass, working of fused silica, mounting cross-wires in microscopes, metal working, small electroplating, calibration of apparatus, repairs, &c. Supervision by an expert and practical training is much more valuable than even elaborate written instructions. There are many useful handbooks specially written on laboratory manipulation and workshop practice which give the operator essential details and numerous hints on the methods of manipulation; but personal practice and expert help is necessary at the beginning. Useful books in this class are:

- Woollatt. *Laboratory Arts*. Longmans, 1934.
- Ansley. *An Introduction to Laboratory Technique*. Macmillan, 1938.
- Walden. 'Laboratory Cements and Waxes', *Sch. Sci. Rev.*, 1937, 21, 212.
- Morton. *Laboratory Technique in Organic Chemistry*. McGraw-Hill, 1938.

Morton's book gives a detailed treatment of practical fundamental operations together with brief descriptions from the literature. Among the chapters are the following headings: drying, melting point, boiling point, distillation (vapour), crystallization, filtration, adsorption, extraction, with about 400 references.

*Physikalische Methoden im Chemischen Laboratorium*. Verlag Chemie, 1937.

This book deals with a variety of technique of an advanced nature, e.g. X-ray analysis, selective adsorption, Raman effect, dielectric measurements, polarographic methods of analysis, &c.

## S. 1. Glass-Blowing

Recent references to many books on this subject are given in Strong's book. Aid is given in the design and construction of research apparatus and in the art of moulding and casting with the elements of shop and foundry practice. Chapters on glass-blowing in the making of optical parts are also included. The early small laboratory manual of Shenstone on the methods of glass-blowing and silica working (Longmans)



although old can compare favourably with many more recent works. Turner's book consists of a series of papers on the nature of glass and quartz and their physical properties. A more comprehensive and recent volume has been written by Morey.

Strong (with collaborators). *Procedures in Experimental Physics*. Prentice-Hall, 1938.

Turner (ed.). *The Constitution of Glass*. Soc. of Glass Technology, Sheffield, 1927.

Morey. *The Physical and Chemical Properties of Glass*, A.C.S. Monograph No. 77. Reinhold Pub. Co., 1939.

Nokes. *Modern Glass Working and Laboratory Technique*. Heinemann, 1937.

Carl Woytacek. *Lehrbuch der Glasbläserei*. 1932.

Frary, Taylor and Edwards. *Laboratory Glass Blowing*. McGraw-Hill, 2nd ed., 1928.

Waugh. *The Art of Glass-Blowing*. Birmingham, 1938.

Periodicals: *Journal of the Society of Glass Technology*; *The Glass Industry* (American trade journal); *Journal of the American Ceramic Society*; *La Céramique*; *Zeitschrift für die Keramischen Glas-und verwandten Industrien*.

### S. 2. Fused Quartz, &c

*About Vitreosil*. The Thermal Syndicate, London, 1937.

Bradley. 'Fused Quartz Spring in a Manometer for Corrosive Gases', *J. Sci. Inst.*, 1938, 15, 338.

Walden. 'Fused Quartz Fibres, Manufacture and Manipulation for Instrument Suspensions', *J. Scient. Inst.*, 1937, 14, 257.

Hunter and Pearce. 'A Heavy Current Hydrogen Discharge Tube', *J. Sci. Inst.*, 1936, 13, 403. Cf. also Garton. *Proc. Phys. Soc.*, 1939, 15, 551.

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Weber and Bazzoni. 'Sealing of Fused Quartz Window to a Pyrex Tube', *Rev. Scient. Inst.*, 1937, 8, 170.

Jones. 'Fused Quartz—Glass-Metal Seals. Fundamental Principles of Construction', *Philips Tec. Rev.*, 1938, 3, 119.

Downsbrough. 'Drawing of Fused Fibre', *Phys. Rev.*, 1937, 51, 877.

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George. 'Two Properties of Silica Glass', *Compt. rend.*, 1927, 184, 1046.

Trostel. 'X-ray Analysis of Devitrification Process', *J. Amer. Chem. Soc.*, 1936, 19, 271.

Birch. 'Mechanical Properties of Fused Quartz', *J. App. Phys. (U.S.)*, 1937, 8, 129.

Dawihl and Rix. 'Tensile Strength of Fused Quartz Rods and Bulbs', *Zeit. f. Tech. Phys.*, 1938, 10, 294.

Von Beaulieu Marconnay und Frantz. 'Quarzgut', *Die Chem. Fabr.*, 1936, 9, 299.

Anderegg. 'Tensile Strength of Fused Quartz Fibres', *Ind. Eng. Chem.*, 1939, 31, 295.

Volerovitch and Leontieva. 'Viscosity of Fused Quartz', *J. Soc. Glass Tec.*, 1936, 20, 139.

Palmer. 'Adsorption on Fused Silica Surfaces', *Proc. Roy. Soc. (A)*, 1937, 160, 254.

Moore and Brown. 'Permeability of Fused Silica to Air at various Temperatures', *J. Soc. Chem. Ind.*, 1939, 58, 142T.

### S. 3. Cleaning of Mercury

'Distillation Plant for Cleaning of Mercury', *Elect. Rev.*, 1938, 123, 119.

'Automatic Distillation Apparatus and Filtering Device for Mercury', *Elect. Rev.*, 1938, 123, 218.

Prausnitz. 'Purification of Mercury by allowing it to fall in Drops through Nitric Acid containing Mercurous Nitrate. A sufficient depth of Mercury is placed in a wide-rimmed Large-pored Glass Filter Crucible, fitting into top of Vertical

- Tube to produce a Fine Spray, the Acid-level being above the Filter Disc', *Chem. Ztg.*, 1939, 63, 54.
- Bates and Baker. 'Purification of Mercury by Heating in Vacuo at 260° for some time', *Proc. Phys. Soc.*, 1938, 50, 409.
- Easly. 'Rapid Purification of Mercury by shaking with Mercurous Nitrate Crystals in the presence of Water, washing with Water and passing through Towelling to Dry', *Ind. Eng. Chem. (Anal.)*, 1937, 9, 82.
- Simeon. 'Mild Steel Variable Slit Filter for Removing Dirt from Mercury', *J. Sci. Inst.*, 1937, 14, 315.
- Monch. *Vacuumtechnik im Laboratorium*. Wagner, Weimar, 1937.
- Espe and Knoll. *Werkstoffkunde der Hochvakuumtechnik*. Springer, Berlin, 1936.

#### S. 4. Determination of Melting-Point

In Morton's book detailed consideration is given to a number of laboratory operations. One complete chapter of 29 pages deals with various practical aspects of melting-point technique. Consideration is given to such points as tubing of substance, rate of heating, mixed melting-points, multiple melting-points, decomposition at melting-point, copper blocks, thermometers, micro-methods, the curve method, the heating curve, &c., with full details of apparatus and manipulation.

- Morton. *Laboratory Technique in Organic Chemistry*. McGraw-Hill, 1938.
- Sinnatt and others. 'The Fusion Point of Coal Ash', *Sci. and Pract.*, 1933, 12, 271.
- Liebhaufsky, Rochow and Winslow. 'The Melting-Point of Barium Molybdate', *J. Amer. Chem. Soc.*, 1939, 69.

#### S. 5. Determination of Boiling-Point

In Morton's book there is a chapter of 22 pages on standard references—micro and macro methods considered. Smith and Wojciechowski by means of a standard differential ebulliometer have developed a very accurate method of boiling-point determination and especially of determining the difference in boiling-points of two closely related substances, e.g. they have used the method to determine the difference in boiling-points of dilute aqueous solutions of deuterium oxide. They have also applied the method to various homologous series of organic compounds. The normal boiling-point it is claimed can be obtained with an accuracy of  $\pm 0.002^\circ \text{C}$ . A somewhat different apparatus is used by Swietoslawski. A full account of the work is given in a publication by this worker with over 70 references to the literature of the subject.

- Morton. *Laboratory Technique in Organic Chemistry*. McGraw-Hill, 1938.
- Smith and Wojciechowski. *J. Res. Nat. Bur. Standards*. 1936, 17, 841.
- Wojciechowski and Smith. *Roczniki Chem.*, 1937, 17, 118.
- Swietoslawski. *Ebulliometry*. 2nd ed., Chem. Pub. Co., New York, 1937.

#### S. 6. Hydrogenation

- Hilditch and Hall. *Catalysis in Theory and Practice*. Chapman & Hall, 1937.
- Dean and Hilditch. *Utilization of Fat*. Harvey, 1938 (with bibliography).
- Ellis. *Hydrogenation of Organic Compounds*. Routledge, 1931.
- Maxted. *Catalysis and its Industrial Application*. Churchill, 1933.
- Adkins. *Reactions of Hydrogen with Organic Compounds*. Univ. Wisconsin Press, 1937.
- Armstrong. 'Hydrogenation in Practice and Theory and the Manufacture of Hydrogen', *Trans. Inst. Chem. Eng.*, 1931, 139, 9.
- Fraser. 'General Review on Nickel as Catalyst', *Trans. Electrochem. Soc.*, 1937, 71, 91.
- Curt. *Studien zur katalytischen Hydrierung von Cyanverbindungen: Die katalytische Hydrierung des Amygdalins*. (28 pp.) St. Louis, Alsatia, 1937.
- Committee of Imperial Defence: Report of Subcommittee on Oil from Coal. 1938.

#### S. 7. Photography

Photography has varying applications in many branches of practical physical chemistry. There are numerous books on the subject that cover the general require-

ments of the scientific worker, and the following short list has been selected from these books :

Clerc. *Photography, Theory and Practice*. Pitman, 1937.

Neblette. *Photography, Its Principles and Practice*. 3rd ed., Chapman & Hall, 1937.

Mees. *The Fundamentals of Photography*. 8th ed., Kodak, 1938.

Blair. *Practical and Theoretical Photography*. Pitman, 1939.

Hay and Rohr. *Handbuch der wissenschaftlichen und angewandten Photographie*. Springer, 1923-33.

Any one of the general texts quoted gives a good account of photographic process generally—especially from the practical aspect. The authors have personally found the volume by Neblette very helpful even on special problems. Emulsions and the latent image, as well as the sensitometry of photographic material are studied, while details of practical manipulation of cameras and the working of photographic methods, negative and positive, are fully dealt with.

In Eder's book the whole science of photography is discussed. From time to time new parts appear. Thorpe (*Dict. of Chemistry*) has a comprehensive article on Photography especially from the standpoint of the chemist. See also section on Colorimetry and Infra-red. A review of the field of Photography patents and other advances is available in English, French and German.

Mees. 'Photography and the Advance of Pure Science', *J. Frank Inst.*, 1938, 226, 281.

Crabtree and Matthews. *Photographic Chemicals and Solutions*. Chapman & Hall, 1939.

Eder. *Ausführliches Handbuch der Photographie*. Knapp, 4th ed. began to appear 1926—new parts from time to time.

Bloch. *Criminal Investigation and Evidence by Photography*. Ilford, 1937.

Spencer. *Colour Photography in Practice*. Pitman, 1938.

Dunn. *Natural Colour Processes*. 2nd ed., Chapman & Hall, 1938.

Coote. *Making Colour Prints*. London, Focal Press, 1939.

*Photographic Abstracts* of the Royal Photographic Society (quarterly).

*The British Journal of Photography* reviews the field of Photographic Patents in English.

*Bulletin de la Société française de photographie* and *Science et Industries Photographiques* review French advances.

*Zeitschrift für wissenschaftliche Photographie*, *Photophysik und Photochemie* and the annual *Jahresberichte der Photographie*.

#### CHAPTER IX. HIGH PRESSURE TECHNIQUE

Some of the publications mentioned in this list are not confined to high pressure methods and their applications, but certain chapters or volumes deal with the subject.

Bone, Newitt and Townend. *Gaseous Combustion at High Pressures*. Longmans, 1929.

Bridgman. *The Physics of High Pressure*. Macmillan, 1931.

Macted. *Catalysis and its Industrial Applications*. Churchill, 1933.

Tongue. *The Design and Construction of High Pressure Chemical Plant*. Chapman & Hall, 1934.

Nash and Howes. *The Principles of Motor Fuel Preparation and Application*. Chapman & Hall, 1934.

Ipatieff. *Catalytic Reactions at High Pressures and Temperatures*. Macmillan, 1936.

Adkins. *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts*. Wisconsin, 1937.

*Transactions of the Chemical Engineering Congress of the World Power Congress, London, 1936*. Lund Humphries, London, 1937. (Vols. I and III.)

Tongue. *A Practical Manual of Chemical Engineering*. Chapman & Hall, 1939.

Eucken und Jakob. *Der Chemie-Ingenieur*. Band III. Vierter Teil Hochdruckoperationen. Acad. Verlag Leipzig, 1939.

## CHAPTER X. THERMOMETRY

There is considerable activity in the field of temperature recording and no attempt can be made here to give a summary of recent work. In *Science Abstracts* (Physics) there is a separate section on Temperature, and an excellent abstract is given monthly of all new work in this subject (see Introduction).

In April, 1939, provisional arrangements were made by the American Institute of Physics to hold at a later date a symposium on Temperature, Its Measurement and Control in Science and Industry.

The Reports on Progress in Physics for 1937 and 1938 of the Physical Society (London) contain two sections on the measurement of temperature and part of the general treatment of the subject Heat.

Powell. 'Temperature', 1937, 4, 76.

Powell. 'The Measurement of Temperature', 1938, 5, 168.

Both of these articles give numerous references to the literature.

Wensel. 'International Temperature Scale and Some Related Physical Constants', *J. Res. Nat. Bur. Standards*, 1939, 22, 4.

Kurte and Simon. '"Curie" Scale of Temperature', *Phil. Mag.*, 1938, 26, 849.

Hoffmann und Tingwaldt. *Optische Pyrometrie*. Braunschweig, 1938.

## CHAPTER XI. THERMOCHEMISTRY

*S. 1. Thermal Measurements*

The International Critical Tables contain a large amount of thermochemical data completed mostly from papers earlier than 1930. The Smithsonian Tables, 8th revised, 1933, give tables on Thermal Conductivity, Coefficients of Expansion, Specific and Latent Heat and Thermometry. Biochowsky and Possini have reviewed all the published thermochemical data involving heats of reaction (excluding carbon compounds of three or more carbon atoms) and have prepared therefrom a self-consistent table of 'best' values for the heats of formation of the chemical substances. The tables contain 5,840 values of heats of formation, and, in addition, 350 values of heats of transition, fusion, vaporization, or reaction for substances for which the heat of formation is not known. Description is given of the physical state of each substance. In the list of 3,730 references are given the citations to the literature for all the published works bearing on thermochemistry which are mentioned or discussed in the text. This list includes all the publications covered by *Chemical Abstracts* up to January 1st, 1931, and nearly all of the important and significant contributions which have been published in the period from January 1st, 1931, to January 1st, 1934.

From the thermochemical values given in the tables, one can compute heats of solution, dilution, transition, fusion, vaporization, sublimation, precipitation, neutralization, combustion, ionization, excitation, dissociation, &c.

For a full list of abstracts see section on Heat in *Science Abstracts* especially for reference to Specific Heats, Latent Heat of Vaporization, and Heat Conductivity. The conduction of heat is also reviewed by Powell.

Bichowsky and Rossini. *The Thermochemistry of the Chemical Substances*. Reinhold, 1936.

Powell. 'Conduction of Heat', *Reports of Progress in Physics* (Phys. Soc., London), 1938, 5, 174.

Clarke and Stegeman. 'Heat of Combustion of Mono- and Disaccharides', *J. Amer. Chem. Soc.*, 1939, 61, 1726.

Brutzeus. 'Thermochemistry of Nitrogen Compounds', *Compt. rend.*, 1939, 208, 997.

*S. 2. Bomb Calorimetry*

Aston and Eidinoff. 'Low Temperature Precision Adiabatic Calorimeter', *J. Amer. Chem. Soc.*, 1939, 61, 1533.

- Carpenter and Bryant. 'High Temperature Vacuum Calorimeter of the Copper Block Type', *J. Sci. Inst.*, 1939, **16**, 183.  
 Perlick. 'Vacuum Calorimeter', *Z. Ges. Kaltenindustr.*, 1937, **44**, 201.  
 Fontell. 'Differential Calorimeter', *Soc. Scien. Fennica Comm. Phys. Maths.*, 1938, **10**, 1 (*Sc. Abs.*, A, **42**, 494, 178).  
 Powell. 'Calorimetry and Specific Heats', *Report of Progress in Physics*, 1938, **5**, 170. Roth. 'Recent Progress in Calorimetry and Thermochemistry', *Zeit. f. Elektrochem.*, 1939, **45**, 335. (A general survey of experimental work for the past four years.)

For further references see *Science Abstracts* (A, Physics), section on Calorimetry under Heat.

### S. 3. Gas Calorimetry

The calorific values of gases at low temperatures (for specific heat determinations) are generally determined by the continuous flow method or the Nernst-Eucker method using compressed gas. For an example of the continuous flow method see Hesse, *Zeit. f. phys. Chem.*, 1929, **4**, 142. The second method was used for the examination of hydrogen by Eucker and Hiller (*ibid.*). Powell gives a bibliography of recent work in this subject to the end of 1936.

- Boys. 'My Recent Progress in Gas Calorimetry', *Proc. Phys. Soc.*, 1936, **48**, 881.  
 Hyde and Mills. *Gas Calorimetry*. Benn, 1932.  
 Powell. 'Calorimetry and Specific Heats', *Report Prog. Physics*, Vol. IV, 1937.  
 Jackson. *Low Temperature Physics*. Methuen, 1934.  
 Jost. 'Mechanismus von Explosionen', *Z. Elektrochemie*, 1935, **41**, 183, 232.

### S. 4. Low-temperature Measurement and Production

For fuller references to liquid helium, super-conductivity, heat capacity of metals at very low temperatures see *Science Abstracts* (A, Physics) section on Heat (subdivisions: Conduction, Temperature, and Thermochemistry).

- Jackson. *Low Temperature Physics*. Methuen, 1934. This has 25 references on the production and measurement of low temperatures up to 1933.  
 Hoge and Brickwedde. 'Establishment of a Temperature Scale for the Calibration of Thermometers between 14° and 83° K.', *Bur. of Standards J. of Res.*, 1939, **22**, 351.  
 Simon. 'Determination of Temperatures below 1° K.', *Sci. Prog.*, 1939, **34**, 1933.  
 Williams. 'The Production and Measurement of Low Temperatures', *Sch. Sci. Rev.*, 1937, **19**, 33.  
 Kapitza. 'Liquefaction of Helium by an Adiabatic Method', *Proc. Roy. Soc. (A)*, 1934, **147**, 860.  
 Ruhemann. *Low Temperature Physics*. Camb. Univ. Press, 1937.  
 Crawhall and Kantorowiz. *Very Low Temperatures*. H.M. Stationery Office, 1937.  
 Gutsche. 'Thermal Properties of Liquid Helium', *Zeit. f. phys. Chem.*, 1939, **184** (1), 45.  
 Allen and Jones. 'Liquid Helium', *Nature*, 1939, **143**, 227.  
 Daunt and Mendelssohn. 'Transfer Effects in Liquid Helium', *Proc. Roy. Soc. (A)*, 1939, **170**, 423.

## CHAPTER XII. OTHER PHYSICAL MEASUREMENTS

### SS. 2 and 3. Density

- Tabt. and Malm. 'Determination of Small Differences in Densities (1 part in 10,000)', *J. Phys. Chem.*, 1938, **42**, 1187.  
 Swift. 'Densities of D<sub>2</sub>O—H<sub>2</sub>O Mixtures', *J. Amer. Chem. Soc.*, 1939, **61**, 198.  
 Greenwood and Voskuyl. 'Deuterium—Protium Ratio. Part I. Densities of Natural Waters', *J. Amer. Chem. Soc.*, 1939, **61**, 1342.  
 Culbertson and others. 'The Densities of Fine Powders', *J. Amer. Chem. Soc.*, 1937, **59**, 306; 1938, **60**, 2695.

- Harasima. 'Relations between Changes of Density and Heat of Fusion at the Melting Point of Metals', *Phys. Math. Soc. Japan*, 1938, 20, 850.  
 Abstracts in *Science Abstracts*, 1939, 42, 493, 80.  
 Dodd. 'Density and Surface Tension by the Capillary Elevation Method', *Phys. Rev.*, 1935, 48, 487.  
 Gickehorn. 'Simple Micro-method for determining Specific Gravity of Liquid and Solid Bodies', *Mikrochem.*, 1937, 221.  
 Density and Specific Gravity. British Standard Specification No. 733, 1937, Density Bottles. B. Spec. No. 734, 1937, Density Hydrometers.

#### S. 4. Coefficient of Thermal Expansion

- Lucas. 'Thermal Expansion of Liquids', *Compt. rend.*, 1938, 207, 900.  
 Basu and Maitra. 'Thermal Expansion of Rock Salt by X-ray Reflection', *Ind. J. Phys.*, 1938, 12, 305.  
 Aoyama and Ito. 'Thermal Expansion of Nickel-Copper Alloy at Low Temperatures', *Tohoku Univ. Sci. Report*, 27, 348, 364; and *Sci. Abstracts* (Physics), 1939, 42, 497, 504.  
 Robertson and Ubbelohde. 'Structure and Thermal Properties Associated with some Hydrogen Bonds in Crystals. Part I. Isotope Effect. Part II. Thermal Expansion', *Proc. Roy. Soc. (A)*, 1939, 170, 22.  
 Stokland and others. 'Dilatation of Heavy Water', *Trans. Far. Soc.*, 1939, 35, 312.  
 Trombe. 'Estimation of Quartz by Differential Thermal Analysis', *Compt. rend.*, 1938, 207, 1111.  
 Saunders. 'Improved Interferometric Procedure with application to Expansion Measurements', *Bur. of Standards, J. of Res.*, 1939, 23, 179.

#### S. 5 Surface Tension

In the *Reports of Progress in Physics*, Vol. 4, 1938, and Vol. 5, 1939, of the Phys. Soc. London there are two articles by Brown on 'Surface Tension'—they both have a large number of references to the current literature.

- Jones and Ray. *J. Amer. Chem. Soc.*, 1937, 59, 187.  
 McBain and Swain. *Proc. Roy. Soc. (A)*, 1936, 154, 608.  
 Ferguson and Kennedy. *Phil. Mag.*, 1938, 26, 41.  
 Fisher and Mackay. 'Surface Tension of Dilute Solutions', *Canadian J. of Res.*, 1938, 16, 11, 207.  
 Katz and Saltman. 'Surface Tension of Hydrocarbons', *Ind. Eng. Chem.*, 1939, 31, 91.  
 Guastalla. 'Surface Tension Manometer with Pendulum Suspension', *Compt. rend.*, 1939, 208, 973.  
 Brown. 'Surface Tension', *Reports of Progress in Physics*, Vol. 4 (1938), Vol. 5 (1939).  
 Parmelee, Lyon and Harman. 'The Surface Tensions of Molten Glass', *Univ. of Illinois Bulletin*, 1939.  
 Ferguson. *Surface Tension*. Methuen (in preparation).

#### S. 6. Monomolecular Films

- Alexander. 'Use of Monolayer Measurements for Determining Structure in Aqueous Media', *J. Chem. Soc.*, 1939, 177.  
 Dervichian and Joly. 'Transformation of Higher Orders in Monomolecular Films', *Compt. rend.*, 1939, 208, 1468.  
 Adam, Askew and Parkhurst. 'Interactions between Adsorbed Substances of Simple Constitution and Insoluble Monolayers', *Proc. Roy. Soc.*, 1939, 170A, 485.  
 Hawkins and Florence. 'Molecular Interaction in Mixed Monolayers. Part I. Mixtures of Alcohols, Acids and Amides. Part II. Unstable Mixtures of Unsaturated Acids', *J. Chem. Phys.*, 1938, 6, 847.  
 Langmuir. 'Molecular Layers', *Proc. Roy. Soc.*, 1939, 170A, 1.

S. 7. *Viscosity*

- Barr. *Report of Progress in Physics*. 1936, 3, 23.  
 First Report on Viscosity and Plasticity by a Committee of the Acad. of Sc., Amsterdam (1935). Second Report, Nordemann Pub. Co., New York, 1938.  
 Ubbelohde. *Zur Viskosimetrie*. 2nd ed., Hirzel, Leipzig, 1937.  
 Spells. 'Viscosity of Liquid Gallium over a Wide Range 30° C. to 1100° C.', *Proc. Phys. Soc.*, 1936, 48, 299.  
 Goodeve. 'The Viscosity of Non-Newtonian Fluid', *Report of Progress of Physics*, 1938, 5, 20. This article gives a bibliography to the end of 1938.  
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 Salceanu. 'Determination of Viscosity of Liquids', *Compt. rend.*, 1939, 208, 1797.  
 Ribaud and Vasilescu. 'Viscosity of Gases at High Temperatures', *Compt. rend.*, 1939, 208, 1884.  
 Itterbeck and Claes. 'Viscosity of H<sub>2</sub> and D<sub>2</sub>', *Physica*, 1938, 5, 938.  
 Weber. 'Viscosity of Gases', *Physica*, 1939, 6, 551.

S. 10. *Elasticity, etc.*

- Cox. 'Elasticity', *Reports of Progress in Physics*, 1938, 5, 12.  
 Houwink. *Elasticity and Structure of Matter*. Cambridge, 1937.  
 Hanemann and Schrader. *Atlas Metallographicus*. Sections 5 and 6. Berntraeger Verlag, Berlin, 1939.  
 Hinz. 'Elastic Deformation of Rochelle Salt', *Zeits. f. Phys.*, 1939, 111, 9, 617.  
 Bender. 'Elasticity of Monocrystalline Alkali Metals at Low Temperatures', *Ann. d. Phys.*, 1939, 34, 4, 359.  
 Houwink and Heinze. 'Plastometry of Synthetic Resins', *Ind. Eng. Chem.*, 1938, 10, 680.  
 Fischer. *Laboratoriumsbuch für die organischen plastischen Kunstmassen*. Halle, 1938.  
 Nieuwenburg. Second Report on Viscosity and Plasticity, *Proc. R. Acad. Sc., Amsterdam*, 1938.

## CHAPTER XIII. MOLECULAR PROPERTIES

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 Briegleb. *Zwischenmolekulare Kräfte und Molekülstruktur*. Enke Stuttgart, 1937.  
 Stuart. *Molekülstruktur: Bestimmung von Molekülstrukturen mit physikalischen Methoden*. Berlin, 1934.  
 Debye. *Methode zur Bestimmung der elektrischen und geometrischen Struktur von Molekülen*. Hirzel Leipzig, 1937.  
 Ulmann. *Molekülgrößen-Bestimmungen hochpolymerer Naturstoffe*. Dresden-Leipzig, 1936.  
 Kremann. *Zusammenhänge zwischen physikalischen Eigenschaften und chemischer Konstitution*. Dresden-Leipzig, 1937.

S. 1. *Solubility*

- Gibson. 'Effect of Pressure on the Solubility of Solids in Liquids', *J. Amer. Sci.*, 1938, 35A, 49.  
 Putnam and Kobe. 'Ethylene Diamine as an Ionising Solvent', *Trans. Electrochem. Soc.*, 1938, 74, 609 and 623.  
 Wiebe and Gaddy. 'Solubility of CO<sub>2</sub> in Water at 50, 75 and 100°, and at Pressures up to 700 Atm.', *J. Amer. Chem. Soc.*, 1939, 61, 315.  
 Moll. 'Influence of Organic Solvents on High Molecular Materials', *Kolloid Zeits.*, 1939, 86, 1.  
 Scratchard, Hamer, and Wood. 'Isotonic Solutions. Part I. Chemical Potential of Water in Aqueous Solutions', *J. Amer. Chem. Soc.*, 1938, 60, 3061.

Holmes. 'Increasing Solubility of Oils in Water-Soap Systems', *J. Phys. Chem.*, 1939, 43, 495.

Schulz. 'Solubility of High Molecular Substances', *Z. f. phys. Chem.*, 1939, 184, 1.

SS. 2 and 3. *Molecular Weights*

Bodenstein. 'Dependence of our Knowledge of Atoms and Molecules on the Development of Technique and Apparatus', *Naturwiss.*, 1938, 26, 833.

Neumann and Lichtenberg. 'Molecular Weight and Vapour Pressure of Se', *Z. f. phys. Chem.*, 1939, 184A, 89.

Batuecas. 'Ramsay and Steele's Vapour Density Measurements', *Z. f. phys. Chem.*, 1939, 183A, 438.

Koteswaran. 'Molecular Association in Fatty Acids', *J. Chem. Phys.*, 1939, 88.

Samigan. 'Use of Refraction for Determining Molecular Weight', *J. Chem. Phys. Russ.*, 1936, 8, 845.

Lin and Chou. 'Modification of Rast's Micro-Method for Molecular Weight Determination', *J. Chinese Chem. Soc.*, 1936, 4, 422 (see *British Chem. Abstracts*, 1937, A1, 100).

'High-speed centrifuges must become an integral part of research laboratories which propose to study proteins or other macromolecular compounds. Fortunately the vacuum-type centrifuges are inexpensive enough to make this possible'—Bream, 'High Speed Centrifuging', *Rev. Mod. Physics*, 10, 259. See Vol. 2, Chap. IV,\* S.2.

Beckmann and Landis. 'Mol. Wt. of  $\beta$ -amylose by Ultracentrifuge', *J. Amer. Chem. Soc.*, 1939, 61, 1495.

Cf. Kraemer. *Ind. Eng. Chem. (Anal.)*, 1938, 10, 128.

SS. 5 and 6. *Rates of Reactions and Mass-Action.*

*Reactions Kinetics*. Faraday Soc., 1937.

Kistiakowsky and Stauffer. 'The Kinetics of Gaseous Addition of Halogen Acids to Isobutene', *J. Amer. Chem. Soc.*, 1937, 50, 165.

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Taradoire. 'Reactions between Solids, II', *Bull. soc. chim.*, 1939, 6, 1249.

S. 7. *Stability of Explosives*

Reilly. *Explosives, Matches and Fireworks*. Gurney & Jackson, 1938.

Kast und Metz. *Chemische Untersuchung der Spreng- und Zündstoffe*. 1931.

Lehalleur. *Foudres, explosives et artifices*. 1935.

Sutton. 'Energy Measurements: Detonation of Tetryl', *Trans. Far. Soc.*, 1938, 34, 992.

Meerscheidt-Hüllessem. 'Determination of Stability of Explosives with aid of the gas buret', *Z. ges. Schiess- u. Sprengstoffw.*, 1939, 34, 167.

The publications of the Bureau of Mines (U.S.A.) contain a number of relevant papers. Technical Paper No. 478 is on the production of explosives; Bulletin No. 346 (1931), by Munroe and Teffany, is on the physical testing of explosives.





# INDEX

*It is intended here to list alphabetically the main topics treated, together with some special items, without making the index so detailed as to be clumsy and ineffective. No attempt is made to include the numerous authors cited. The numbers refer to the pages; when the reference is to the 'Suggestions for Further Reading', the number is in italics. When the page-number is preceded by 'ii.' the reference is to volume ii; otherwise to vol. i.*

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